

THE ELECTROSLAG MELTING PROCESS

By R. H. Nafziger and others
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UNITED STATES DEPARTMENT OF THE INTERIOR
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PREFACE

In the past several years, advances in the development of electroslag melting have stimulated interest in the process among metal producers, both in the United States and abroad. This is evidenced by increased production, by the frequency of national and international symposia devoted to the process and the large attendance at such symposia, and by the attention given to electroslag melting both in the popular metals news media and in articles appearing in professional journals. In view of this, it seems appropriate that an update of several excellent review books be published. It is with such thoughts in mind that this Bulletin was written.

The senior author made his first contact with the process in 1968. Since then, numerous metals and alloys have been electroslag-melted at the Bureau of Mines Albany Metallurgy Research Center. Although emphasis is placed on this Bureau work, brief accounts of related work of others are included in the Bulletin, which cover developments through December 1973.

Numerous people have made this effort possible, as evidenced by the number of contributors herein. Special acknowledgment is due N. Riazance for his many translations, particularly from the Russian literature; A. G. Pike and D. C. Robinson for their operating competence and willingness to attempt any type of melt; and R. A. Beall for his continuous enthusiasm and encouragement.

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THE ELECTROSLAG MELTING PROCESS

by

R. H. Nafziger ¹ and others ²

ABSTRACT

This Bulletin traces the development of the electroslag melting process from its modest beginnings to the present. Important basic mechanisms such as electrochemistry, thermochemistry, and heat transport are described. Since the choice of flux is a unique parameter in the electroslag process, two chapters are devoted to this subject. Electroslag melting experience for reactive metals, base metals, ferrous alloys, superalloys, and the refractory metals, both inside and outside the Bureau of Mines, is outlined. The final two chapters are devoted to a related melting scheme, variations of the process, and what may lie in the future for electroslag melting.

INTRODUCTION

This Bureau of Mines Bulletin updates previous general treatments of the electroslag melting process, although results of work conducted at the Bureau's Albany Metallurgy Research Center are emphasized, pertinent results of work conducted elsewhere are included to give an overall picture of the process and its status.

The electroslag process is a secondary melting technique developed several decades ago, which can be used for a variety of metals and alloys, provided appropriate fluxes and melting parameters are employed. Historical development of the process throughout the world is discussed in chapter 1.

The electrode is usually consumable and is composed of the metal or alloy to be melted. It may be pressed sponge or scrap, or it may be cast or wrought material. Usually, minimal electrode preparation such as descaling or surface dressing is required. The diameter of the electrode is smaller than that of the crucible, although the ratio can vary within relatively wide limits. As practiced in our laboratory, a threaded stub of the same metal or alloy to be melted is welded to the top of the electrode and attached to a movable water-cooled copper electrode support. This in turn is connected to the power supply, which may be either single-phase ac, dc straight polarity (negative), or dc reverse polarity (positive), as shown in figure 1. Three-phase ac may also be used wherein three electrodes are used.

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² The other authors who contributed to this Bulletin are identified in the chapters in which their work appears.

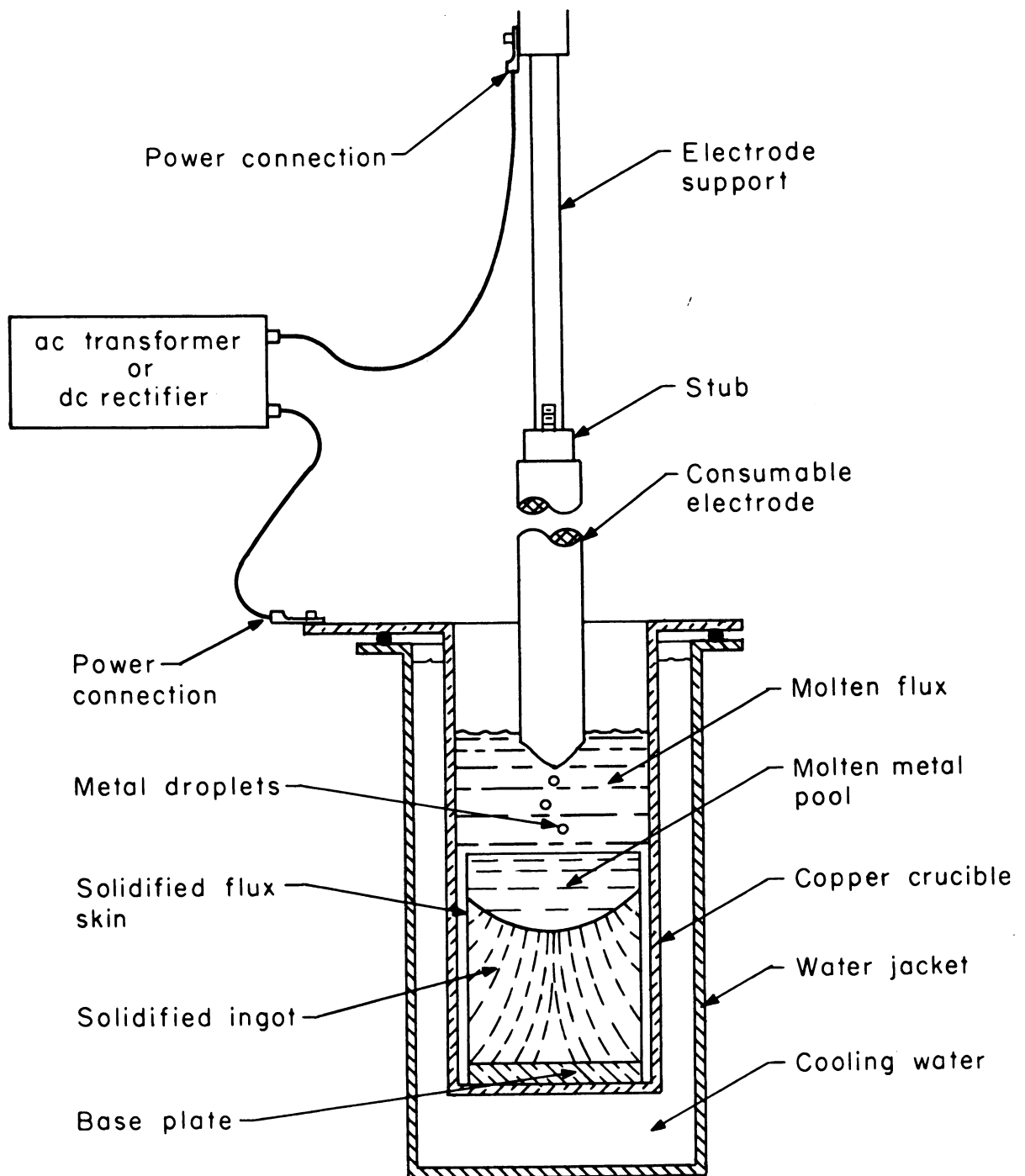


Figure 1.—Schematic diagram of the electroslag melting process.

Before starting, a base plate and/or turnings of the metal or alloy to be melted are placed in the bottom of a water-cooled copper crucible. This crucible is fitted with a flange on top, to which the second power lead is connected.

Present practice calls for charging all or a portion of the dry, prefused flux into the bottom of the crucible around the electrode prior to initiation of the melt.

Additional flux may be charged during the melt through the top of the furnace if an air melt is being conducted, or through a side feeder during a closed-furnace melt.

At the beginning of a melt, an arc is struck between the electrode and the base plate. This is immediately quenched by the fusing flux. As soon as the flux has completely fused, the power is increased, the temperature of the flux reaches and exceeds the liquidus temperature of the electrode, and the electrode begins to melt. Metal droplets collect in a pool on the base plate and begin to solidify. As solidification proceeds, an ingot (secondary electrode) forms with a molten pool of metal on top, beneath the rising bath of molten flux. The molten flux in contact with the water-cooled crucible solidifies during the melt to form a thin skin between the crucible and the solidifying ingot. This skin is responsible for the excellent ingot surfaces attained from electroslag melting. Near the end of the melt, the power can be reduced to eliminate the formation of pipe and centerline porosity.

Chapter 2 discusses the problems associated with electrochemical effects which are produced as a result of current passing between the electrode and the ingot through the molten flux by ionic diffusion. These effects can influence ingot chemistry. Other operating parameters such as furnace atmosphere and flux composition can also influence element partitioning between flux and metal phases and thus alter ingot chemistry. Thermochemical effects at the metal droplet-flux interface may also play a role. These subjects are considered in chapter 3.

During the melting operation, Joule heating of the flux is responsible for heat generation (*1*).³ Nonuniform heat distribution is discussed more fully in chapter 4.

Chapters 5 and 6 are devoted to the discussion of intelligent selection of fluxes depending on the metal or alloy to be melted and the objective of the melt in terms of chemical changes, solidification, and ingot structure.

Numerous advantages of the electroslag process over secondary melting processes have been delineated in the literature. These, together with the effects of many variable electroslag melting parameters, are discussed in chapters 7 through 15; electroslag melting results are presented for reactive metals, base metals, ferrous alloys, superalloys, and refractory metals.

Chapter 16 outlines modifications to the process such as starting with a molten flux, alternate power schemes, molten metal agitation, multiple electrodes and ingots, and nonconsumable electrodes for specific applications such as unusual ingot shapes. An alternate process which does not require electrodes is also described in this chapter. The last chapter is devoted to the future of the process with respect to trends, tonnage, and cost comparisons with other secondary refining processes.

REFERENCE

1. Mitchell, A., and S. Joshi. The Thermal Characteristics of the Electroslag Process. *Met. Trans.*, v. 4, No. 3, March 1973, pp. 631-642.

³ Italicized numbers in parentheses refer to items in the list of references at the end of each chapter.

CHAPTER 1.—HISTORICAL DEVELOPMENT OF THE ELECTROSLAG PROCESS

By R. H. Nafziger

Although a practical electroslag melting process was conceived nearly 40 years ago, its acceptance and development have been remarkably slow in the United States and many Western European countries. This was probably due to prior commitments to more conventional alternative secondary melting processes. Development of the process in the Soviet Union has been more rapid since the relatively expensive dc power supplies and vacuum equipment normally required by comparable processes such as vacuum-arc remelting are eliminated.

The past few years have seen an increase in the acceptance of the process as producers began to realize its advantages for many types of specialty steels and superalloys, although it was estimated that in 1970 electroslag-melted-steel production represented only 0.1 percent of worldwide steel-making capacity (40). The trend toward larger ingot production, complex ingot shapes, and improved casting technology is continuing.

This chapter traces the historical background of the electroslag process to the end of 1972 in countries where independent development occurred. In addition, it shows how this technology has been adopted by installations in numerous other countries. Independent development of the electroslag process has occurred only in the United States, the U.S.S.R., Austria, and the United Kingdom. Installations in all other countries have been constructed using technology developed in these four countries.

UNITED STATES

Although an early patent by Armstrong in 1930 (2) described a small-scale melting process which utilized a flux to prepare ferrous alloy shapes, R. K. Hopkins is credited with inventing the electroslag process in the United States. A mechanical engineer by profession, Hopkins joined the M. W. Kellogg Co. in 1922 and began developing methods to produce pressure vessels by forge and electric welding. Limitations of

this technique with respect to maximum temperatures, diameters, and thicknesses led him to develop a cladding process to prepare thicker walled vessels to resist corrosion by sour crude oil, which was of interest to the Kellogg Co. at that time. The first cladding was laid on a nearly horizontal base as a corrosion-resistant alloy. Melting was attained by means of multiple solid and/or hollow electrodes melting through a flux layer. A veneer of the desired thickness was applied to the base by regulating the electrode spacing, current, voltage, electrode travel, and degree of oscillation. This process, termed the Kelcaloy process, was successful from the standpoint of preparing clad plate of straight chrome (for example, type 410) (11). However, attempts to roll more highly alloyed material (for example, types 317 and 347) resulted in unacceptable cracking.

To alleviate this problem, the slab or ingot was placed in a vertical position. A water-cooled copper plate was positioned in front of the side of the slab to be veneered. Both ends were closed along the sides. This change solved the problem and improved the quality of all grades. The weld metal slowly rose in the intervening space (serving as a mold) as multiple electrodes melted beneath a flux layer. An important feature of this technique included directing the arcs toward the junction between the surface of the molten metal pool and the unfused face of the slab. This insured controlled penetration into the slab for a sound weld and for controlled alloy analysis. Pertinent patents issued to Hopkins are listed in table 1. This technique provided the basis for the Pluramelt process in which six consumable electrodes comprising four steel wire electrodes and two tubular electrodes were precisely fed through a layer of molten flux. Three-phase ac power was used. One 5,000-ampere phase was connected to each of the tubular electrodes, and the four wire electrodes were connected in

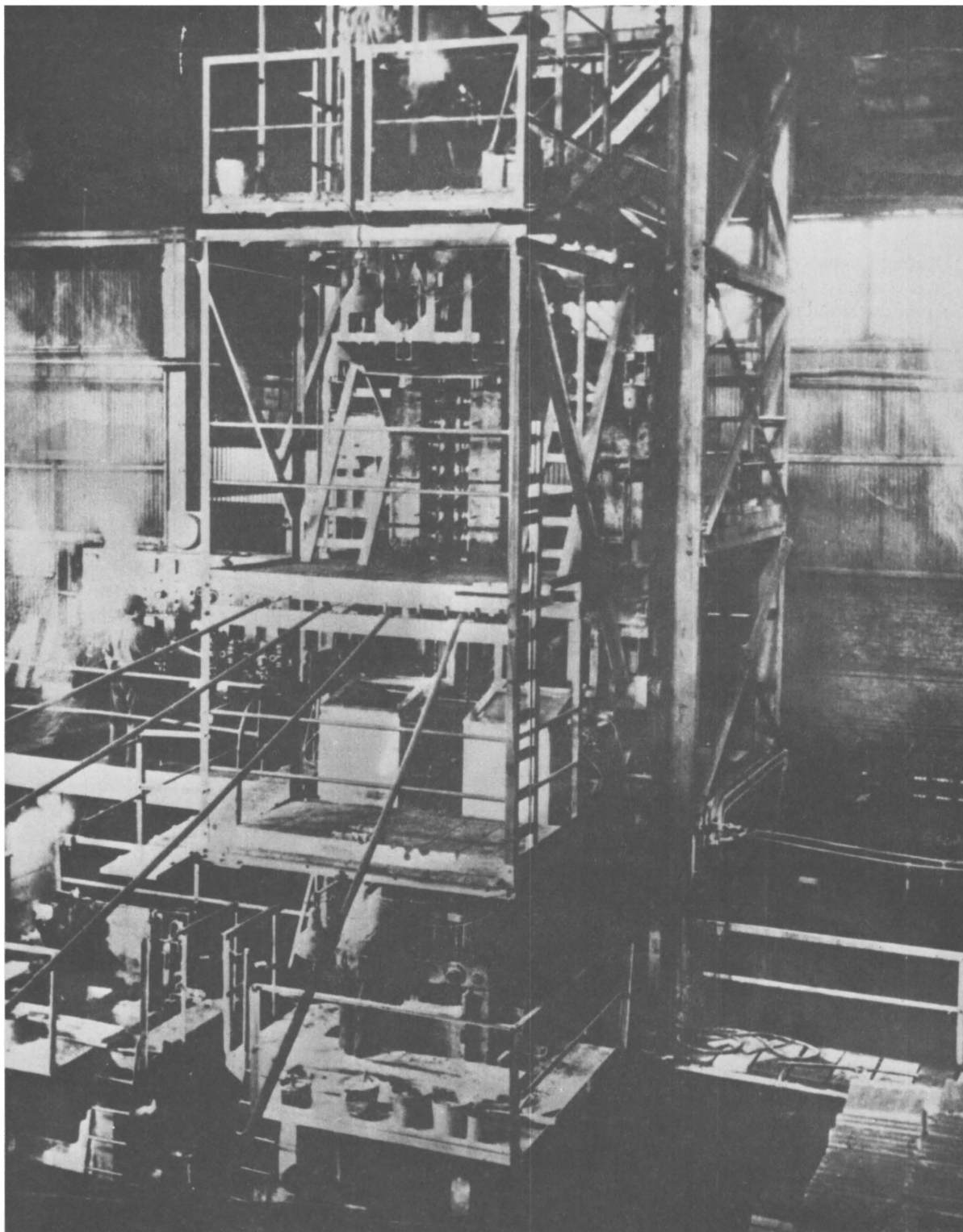


Figure 2.—General view of the Pluramelt machine at Allegheny-Ludlum's Brackenridge plant in 1939 (11, reproduced by permission of TMS-AIME).

parallel to the other 5,000-ampere phase. This process was licensed by the Kellogg Co. in 1939 to Allegheny-Ludlum Steel Corp. for the production of stainless-clad materials, and commercial operation began in December 1939 under Mr. Hopkins' direction.

Figure 2 shows the Pluramelt installation in Brackenridge, Pa. A schematic diagram of this operation is presented in figure 3. To prevent bleeding and cold-shuts, the Pluramelt mold was lined with ladle brick. The flux eroded this brick, and an operator was required to remove the excess volume of resulting slag. A separate nonconsumable electrode controlled the level of the welding machine including the electrodes as it moved up in response to the buildup of weld metal. The key to the success of the Pluramelt

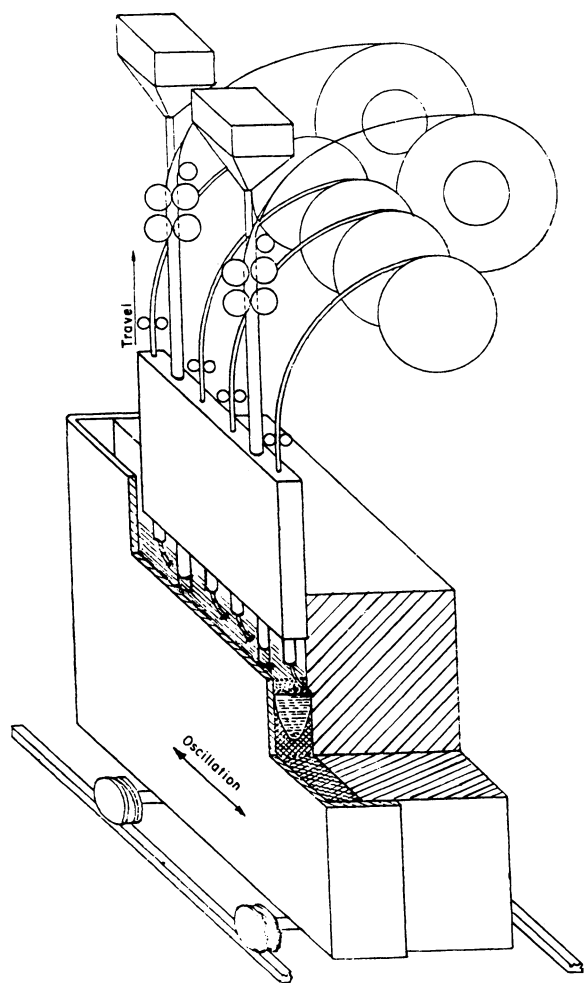


Figure 3.—Schematic diagram of the Pluramelt Process (11, reproduced by permission of TMS-AIME).

process lay in directing the arc to the slab-molten pool interface. Up to seven alloying elements could be introduced.

Table 1.—Selected U.S. patents granted to R. K. Hopkins regarding the electric ingot process and its variations

No.	Issue date	Title	Subject
2,151,914	Mar. 28, 1939	Welding Apparatus	Hollow tubular electrode.
2,191,469	Feb. 27, 1940	Veneering of Metallic Surfaces	Cladding method.
2,191,474	---- do ----	Method for Manufacturing Composite Metal Articles	Cladding in a vertical mold.
2,191,475	---- do ----	Manufacture of Metal Articles	First "canned" ingot.
2,191,479	---- do ----	Manufacture of Alloy Ingots	Electric ingot process.
2,191,480	---- do ----	Apparatus for Manufacturing Alloy Ingots	Do.
2,191,481	---- do ----	Method for Manufacturing Composite Metal Articles	"Pluramelt" cladding method.
2,191,482	---- do ----	---- do ----	Vertical mold cladding method.
2,300,670	Nov. 3, 1942	Electrical Metal Fusing Apparatus and Method	Constant metal feed rate.
2,361,101	Oct. 24, 1944	Metal Casting Apparatus	Level control.
2,370,467	Feb. 27, 1945	Metal Fusing Apparatus and Method	Multiple nonconsumable electrodes.
2,375,107	May 1, 1945	Method and Apparatus for the Continuous Production of Metal	Continuous casting.
2,446,929	Aug. 10, 1948	Method and Apparatus for Electrically Heating Material	Nonconsumable electrode furnace.
3,067,473	Dec. 11, 1962	Producing Superior Quality Ingot Metal	Solid electrode.
3,152,372	Oct. 13, 1964	Method and Apparatus for Producing Improved Alloy Metal	Mold rotation for fine grain size.

Modifications of the Kelcaloy and Pluramelt processes resulted in the development of the first successful electroslag welding technique. The welding was conducted in a water-cooled copper mold composed of sections which were added as the weld progressed vertically.

In 1935, Hopkins invented a process of consumable electrode melting known as the Kellogg electric ingot process. The first patents were issued about 1940 (table 1). Like all of Hopkins' work the process was based on the principle of progressive solidification. This results in more sound and uniform products. A recognized need

for cleaner and less segregated ingots and the expectation that the flux would protect the metal from atmospheric and crucible contamination led to the invention of the process.

The development of the electric ingot process evolved from continuing work on corrosion-resistant veneering. As originally conceived, base material from a coil of strip was fed through a tube mill where it was formed into a continuous tube. This tube was fed into the furnace and served as the consumable electrode. Alloy additions were accomplished by metering appropriate granular alloying elements through another tube of smaller diameter which extended part way down inside the larger electrode tube. Flux additions could also be made through the smaller tube. The alloying elements were added at the rate required to produce the desired composition. Periodically, however, unmelted strip inclusions from the tubular electrode, which had fallen into the molten pool, were found in the finished product. Although modifications partially alleviated this problem, complete elimination of inclusions was not attained. Solid electrodes based on other Hopkins patents were therefore introduced in the early 1950's; the metering devices for alloying elements were retained. Another problem was the inadequate means available to cut continuously cast ingots. Subsequent patents dealt with further refinements of the process. In one variation developed in the late 1930's, a vertical mold or "can" of essentially the same composition of the metal to be melted was placed on a rotating stand which could be withdrawn downward at a rate commensurate to the growth of the enclosed ingot. A patent for this technique was granted to Hopkins in 1940.

A number of variations and modifications followed. These included (1) controlled metering of alloying elements through a hollow tubular electrode, (2) development of single or multiple nonconsumable electrodes to control the liquid level and flux thickness in a vertical mold or for hot-topping and fusing metal, (3) use of balanced three-phase ac power and three solid or hollow electrodes to prepare both cylindrical and slab-shaped ingots (patent 2,191,479, table 1), (4) continuous ingot withdrawal combined with continuous formation from strip of a liner which ultimately became part of the ingot, (5) a rotating mold coupled with an off-center electrode to enhance the development of fine grain structure, (6) electroslag melting under an inert atmosphere at reduced or positive pressures, and

(7) continuous-casting furnaces for ingot production, followed by continuous roll reduction. These techniques are included in a number of patents granted to Hopkins, some of which are listed in table 1. Hopkins has 127 patents credited to him, including 92 from the United States and 35 from 11 foreign countries.

In 1941, the licensing agreement between Kellogg and Allegheny Ludlum was changed to include the electric ingot process. Three ac melting units were then built at Allegheny-Ludlum's Dunkirk plant in 1941. Thousands of tons of high-speed and stainless steels were produced by the Hopkins process during World War II. After the war, demand for steel decreased, and the three Hopkins units at the Dunkirk plant were closed in 1947. At this time, Hopkins returned to Kellogg Co. as director of research, and the firm purchased the three Dunkirk units which were then installed in Jersey City. One such unit is shown in figure 4.

The units were ac operated originally, but troublesome shaking of the hollow electrodes due to harmonic vibration of the 60-hertz frequency caused violent slag eruptions after 9 inches of ingot had been built up. This problem was alleviated by changing to a slag composition with a lower viscosity for the melt start and then adding a more viscous slag with a high CaO content. However, this limited the flexibility of the process to relatively fluid high-speed tool steels, so the three furnaces were changed to dc power for the hollow electrodes in use at that time. Ingots up to 40 cm in diameter could be produced. For many years thereafter, the Kellogg Co. produced a variety of grades of stainless steel by the Hopkins process. Some low-alloy steels were produced where extreme cleanliness was desired. In 1947, the first high-temperature alloy, 16-25-6 (Fe-16Cr-25Ni-6Mo), was successfully melted by the Hopkins process (10). Other processes failed to produce quality 16-25-6. As a result, every turbine wheel for the J-33 engine, numbering over 20,000, was produced in Kellogg's electroslag furnaces. Each wheel was forged from a single 23-cm-diameter, 181-kg 16-25-6 ingot, a number of which are shown in figure 5.

In 1958, Firth Sterling, Inc., was studying vacuum-arc remelting processes and noted the loss of metal due to poor ingot sidewalls and piping. Several electrodes of A-286 air-melted steel were then sent to the M. W. Kellogg Co. for electroslag melting (27). The resulting ingots were so exceptional in surface quality and free

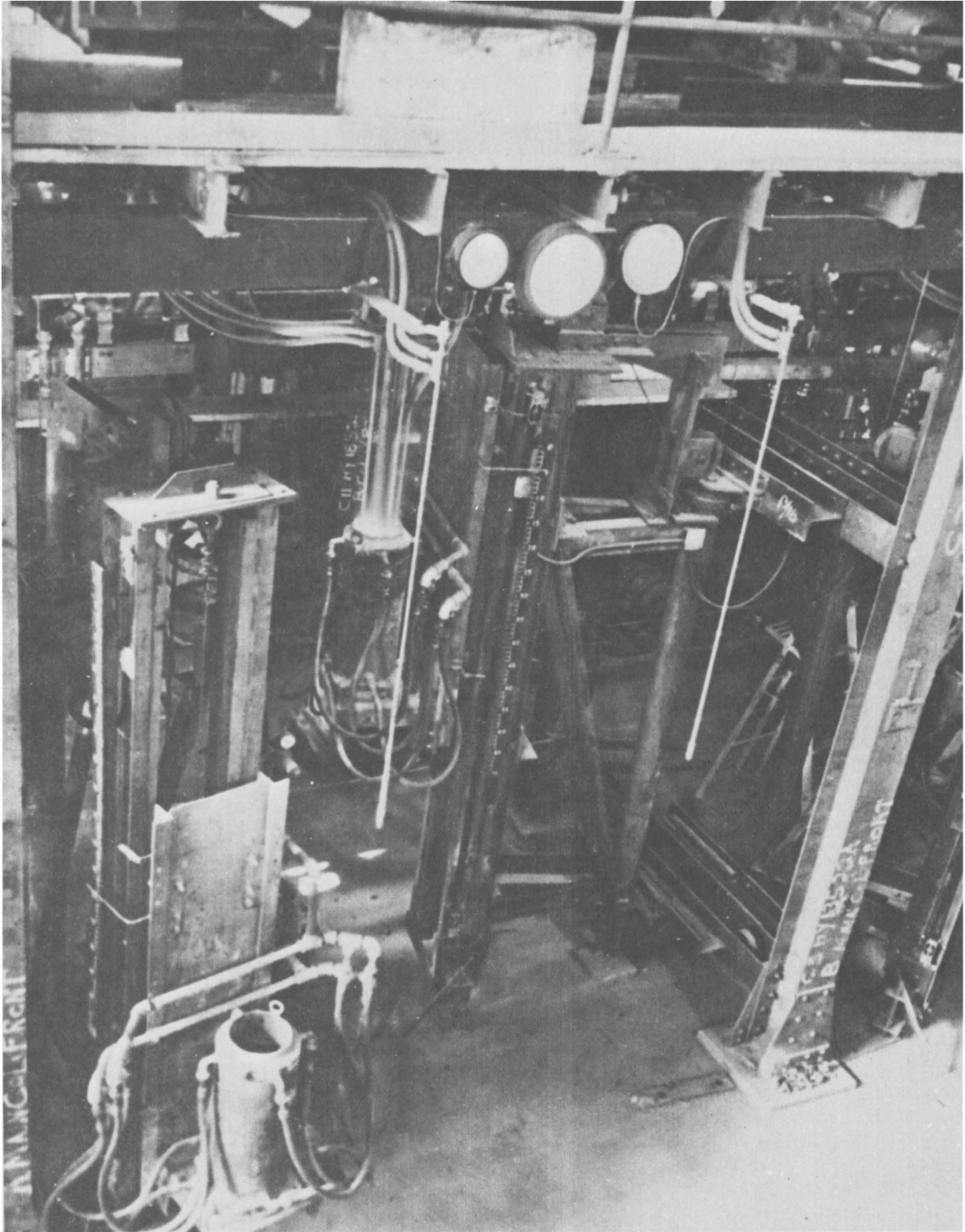
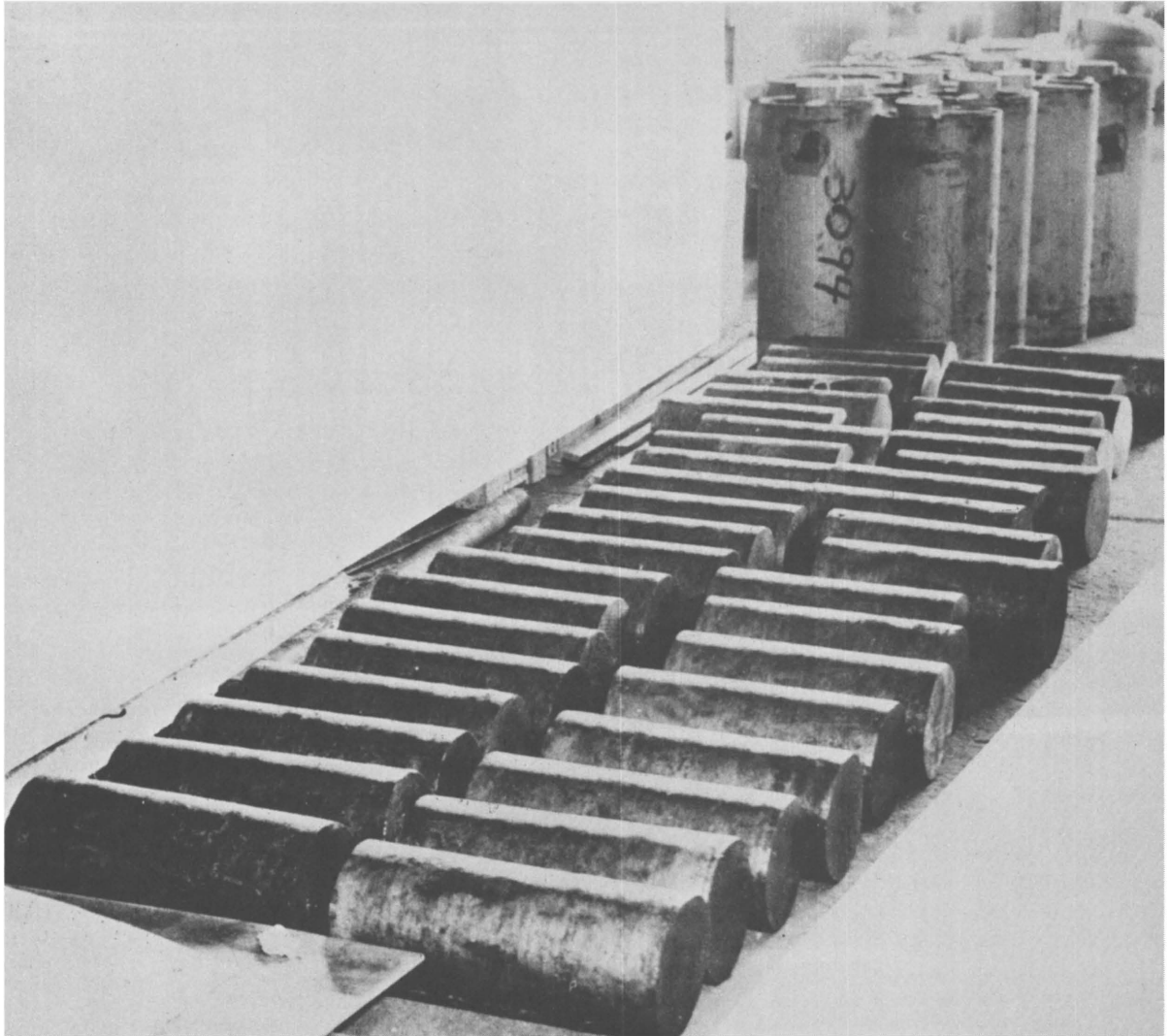


Figure 4.—Electroslag furnace used at Allegheny-Ludlum's Dunkirk plant during World War II and later at the Jersey City plant of M. W. Kellogg Co. Note the auxiliary electrodes in the furnace at center left and the two hot topping electrodes in front. (Courtesy R. K. Hopkins.)



**Figure 5.—Series of 16-25-6 ingots for the J-33 turbine wheel made in the late 1940s.
(Courtesy R. K. Hopkins.)**

of segregation that in 1959 Firth Sterling acquired all rights and patents to the Hopkins process, as well as all equipment. That same year, with R. K. Hopkins as technical director and vice-president, Firth Sterling began production of electroslag-melted high-quality steel ingots up to 50 cm in diameter and 3,600 kg in weight. Grain structure and mechanical properties of typical AISI 9310 and type 304, 347, and 403 stainless steels were said to be excellent (27).

Six years later, Firth Sterling made the patents more readily available through a new licensing arrangement. Licensees could use the process and were permitted to manufacture equipment for the process. In 1965, Union Electric

Steel Corp. was licensed to use the technique, and Lectromelt Furnace Division of McGraw-Edison Co. was granted a nonexclusive license for the design and construction of electroslag melting equipment in the United States (4). Union Electric's plant was built by Heraeus-Engelhard, who had previously obtained an exclusive license to manufacture electroslag equipment outside the United States. Additional Firth Sterling licensees included Carpenter Technology Corp. and Union Carbide Corp.

In 1964, Hopkins retired and became a consultant to Firth Sterling. That same year, Firth Sterling produced its first slab-shaped ingots by the electroslag process. Prior to its purchase by

Teledyne in 1968, Firth Sterling operated four Hopkins furnaces capable of producing 5 million kg of ingot per year. Maximum ingot diameter was 50 cm. Teledyne already had two subsidiaries involved in the electroslag melting process (Vasco and Allvac, BISRA licensees), and so the Firth Sterling plant ceased operations.

In 1965, the Manufacturing Technology Division of Wright-Patterson Air Force Base became interested in the flexibility of the electroslag process as an alternative to the vacuum-arc remelting process and began sponsoring developmental work at Mellon Institute. The Mellon group designed and built its own furnaces based on electroslag welding technology. An 18-percent-nickel maraging high-strength steel, René 41, and Udimet 700 were successfully electroslag-remelted into 10- and 18-cm-diameter and 28- by 50-cm slab-shaped ingots using dc and ac power. Titanium and Ti-6Al-4V sponge was also electroslag-melted into ingots 5 to 9 cm in diameter using CaF_2 fluxes (3). This program demonstrated that the direct conversion of slab-shaped ingots to plate and ring products is feasible. Also produced were hollow ingots of D6 steel by the electroslag process using center mandrels. Air Force sponsorship of the Mellon electroslag work ended in 1971.

The Army Materials Research Agency became interested in the electroslag process for preparing slab-shaped titanium ingots for direct-working operations. In 1965, this agency funded an electroslag program at the Federal Bureau of Mines Albany Metallurgy Research Center. Further details regarding this program are given in chapters 7 and 8. Subsequent in-house electroslag research constitutes the basis for this Bulletin.

In February 1968, an Electroslag Institute was formed, with Henry Shur, a Washington lawyer, as president and G. K. Bhat of Mellon Institute as vice-president and technical director (22). The objective of this institute was to encourage commercialization and scale-up of the electroslag process. Industry members shared in the funding and received improvements in electroslag technology as a result of institute research and development. Two electroslag demonstration furnaces capable of producing 56-cm-diameter ingots were located in Washington, Pa.

Carpenter Technology Corp. began specialty steel production with two new electroslag furnaces in 1971. These furnaces have capacities of the electroslag process to explain the electrical

for producing up to 100-cm-diameter by 180-cm-long ingots. High-speed and special alloy steel ingots are being produced in the movable-mold furnaces. Prior to this installation, the corporation had produced small quantities of electroslag-melted steel in converted vacuum-arc furnaces (16).

By the end of 1972, production electroslag melting facilities in the United States numbered 13 (table 2), based on the best available current information.

U. S. S. R.

After World War II, Soviet scientists at the E. O. Paton Institute of Electric Welding in Kiev were concentrating on the development of the electroslag welding process as a means for improving metal quality and mechanizing the welding of vertical joints. A molten flux bath was used as the heating source, and the entire operation was enclosed in water-cooled copper plates. The Soviets were impressed with the axial crystallization, homogeneity, density, and high purity of the resulting welds. The suggestion was then made to substitute the two end pieces with cooled surfaces and prepare an ingot. The first small ingot of austenitic steel was prepared from 3-mm-diameter welding wire in 1952 (35). From 1952 to 1956, wires up to 6 mm in diameter were used to prepare small alloy ingots with desirable properties. However, the wire feed material was expensive, and therefore the process did not find industrial application (26). The feasibility of using large cross-sectional electrodes was demonstrated in 1956. This, together with an ingot withdrawal scheme, established the ac electroslag melting process in the Soviet Union. At the forefront of this development was Dr. B. I. Medovar, a corresponding member of the Academy of Sciences of the Ukrainian S.S.R., who is presently head of electroslag development at the E. O. Paton Institute of Electric Welding in Kiev. He has been instrumental in developing commercial electroslag furnaces, bifilar ac melting circuits, molten flux starts, and bottom ingot withdrawal techniques. In addition, he and his coworkers have developed several physical models characteristics, heat transfer mechanisms, and ingot structures. The electroslag process was considered by the Soviets as a favorable alternative to the vacuum-arc process, which is used extensively in the United States. Cheaper ac power and no vacuum requirements have been cited as reasons for this preference.

Table 2.—Commercial electroslag melting facilities in the United States

Company	Location	Number and type of furnace(s)	Maximum ingot—		Power	Year of startup	Metals produced	Estimated annual capacity, net metric tons	References
			Diam. cm	Weight kg					
Allegheny-Ludlum Industries, Inc.	Watervliet, N.Y.	2—Converted VAR.	50 each	3,175 each	dc (both)	1969 (both)	Both produce high-speed and stainless steels, high temperature alloys.	6,000 (both)	42
Aztec Metals, Inc.	Monroeville, Pa.	2—Lombard Corp., Accumelt Div.	15, 30	NA	dc (both)	1960–70	Both produce tool and die steels, special alloys (continuous extraction).	6,000 (both)	12, 41
Cabot Corp., Stellite Div.	Kokomo, Ind.	1—Consarc ---	28	900	dc	1963	Iron, nickel, cobalt super-alloys.	6,000–8,000 (all)	41
		1—Consarc ---	40	3,200	dc	1965			
		1—Consarc ---	61	6,400	dc	1967			
		1—Consarc ---	76	12,270	ac	1968			
Carpenter Technology Corp.	Reading, Pa.	1—Consarc ---	61	7,300	(¹)	1971	Tool and die steel, nickel-base alloys.	6,000	15, 7, 39, 41
		2—NRC converted VAR.	50	2,700	dc	1967			
		1—Consarc (lab) VAR/ESR.	20	136	ac	1968			
		1—Dravo (Bohler)	76	16,000	ac ¹	1972			
		1—Dravo (Bohler)	76	16,000	ac ¹	1972			
		1—Dravo (Bohler)	102	23,000	ac	1974			
		1—Dravo (Bohler)	102	23,000	ac	1974			
Cybermetals	Riverton, N.J.	2—Arcos -----	20 by 20 (each)	120, 1,360	ac	1968–69	Both produce tool steels, stainless steels, high-strength steels.	1,125 (both)	41
					ac	1968–69 (both)			
International Nickel Co., Huntington Alloy Products Div.	Huntington, W.Va.	1—Consarc ---	102	18,200	ac ¹	1969	Nickel and nickel-base alloys.	4,500	41
Latrobe Steel Co.	Latrobe, Pa.	1—Converted VAR.	61	6,000	dc	1968	Alloy tool steels.	5,000	38
Lukens Steel Co.	Coatesville, Pa.	1—Consarc ---	76 by 152	16,360	ac ¹	1971	Steel plates and slabs—low-alloy steels (Lectrefine T. M.). Superalloys.	10,000	29
Teledyne Allvac Co.	Monroe, N.C.	1—Heraeus ---	50	6,850	ac	1973		2,500	NA
Union Electric Steel Corp.	Burgettstown, Pa.	1—Heraeus (Fifth-Stirling lic.).	76	4,000	dc	1967	Forged roll compositions.	2,700	41
Universal-Cyclops, Specialty Steel Div.	Bridgeville, Pa.	1—Consarc ---	61	6,800	dc or ac ¹	1970	Tool and die steels, nickel-base alloys (3-station).	2,500	13, 15, 39
Vasco, Teledyne Co.	Latrobe, Pa.	1—Consarc (VAR/ESR).	84	15,900	dc	1966	Tool, bearing stainless, high-alloy steels, iron and nickel-base alloys.	3,350	36, 39, 41
Wallace-Murray Corp., Simond Steel Div.	Lockport, N.Y.	1—Consarc ---	76	14,000	ac ¹	1969	Iron, nickel, and cobalt-base alloys; tool steels.	4,500	36, 39, 41
		1—Consarc (VAR/ESR).	84	15,000	dc	1970		4,000	
		1—Consarc ---	76	15,000	ac ¹	1974		4,200	

NA Not available.

¹ Single-phase ac.

In 1956, the Institute of Electric Welding designed and manufactured a single-phase experimental furnace for industry, designated R-909. Further developments led to the installation in 1958 of the first Soviet commercial industrial

electroslag furnace at the Dnieprospetzstal Works in Zaporozhje. This was a single-phase ac furnace capable of producing ingots up to 25 cm in diameter and 500 kg in weight. Later that year, two three-phase furnaces designed to pro-

Table 3.—Development of Soviet electroslag furnaces

Year	Designation	Maximum ingot—		Power supply	Electrode diam., cm	Remarks and references
		Size, cm	Weight, tons			
1958–59	DSS-1	42.5 diam., 30 square.	1.1	3-phase ac	18	2 3-phase units, each with electrodes and molds. 1st square-cross-section ingot (26).
1959	R-951	42.5 diam.	1.5	Single-phase ac (initially 3-phase).	NA	Movable mold, varied cross-sections, no pits needed (26).
	OKB-905	45 square.	2.5		NA	
1959	EShP-2	60 diam.	2.5	3-phase ac	NA	3 electrodes into 1 crucible (26).
1959–60	EShP-10	120 diam.	10	do.	35	do.
1965–66	EShP-10M	do.	14–15	Single-phase ac	80	
1967–68	U 436	60 x 150	14	3-phase ac	17	Bifilar (see chapter 17), 3 electrodes into one crucible (26).
1968	OKB-906	NA	3.5	NA	NA	
1970	OKB-1065	Square	3.5	Single-phase ac	NA	Similar to EShP-10 (26).
Under construction	OKB-1111	170 diam.	40–60	3-phase ac	150	Analogous to R-951 (26).
	ESR-250 ¹	300 diam.	250	do.	(?)	References 33, 34, 44

NA Not available.

¹ Satisfactory documentation concerning the actual operation of this furnace is lacking.

duce up to 1.5-ton¹ ingots were placed in operation.

Throughout the 1960's, larger furnaces with over 20 variations were designed, manufactured, and placed into operation in the Soviet Union. Several of these variations are treated in chapter 16. Table 3 summarizes the developments. During this time, the Soviets also began exporting their electroslag technology to a number of countries. In May 1969, Patent Management, Inc., obtained exclusive U.S. patent rights and technical knowledge for the Paton electroslag process from V/O Licensintorg, the Soviet licensing agency. The intention was to license U.S. companies and provide equipment designs and operational data. Recently, the Cabot Corp. acquired U.S. patent rights from Patent Management for producing hollow metal ingots by the electroslag process (14).

Several other research institutes in the Soviet Union became involved in electroslag development work in the 1960's. In 1967, the Chelyabinsk Research Institute began work on physical property comparisons between electroslag and more conventionally remelted alloy steels. Zlatoust and Chelyabinsk Iron and Steel Works have conducted work to optimize electrode parameters. Another electroslag plant is Elektrostal Metallurgicheskyy Zavod Noginsk near Moscow (40).

Soviet production of electroslag-melted ingots has increased substantially in the past decade. In 1964, an annual production of 100,000 tons of over 75 grades of steel was reported (40). This was doubled in 1966. In 1970, the estimated annual production in the Soviet Union was over

400,000 tons of more than 200 grades of steel. At the Dnieprospetsstal Works in Zaporozhje, at least 16 electroslag furnaces are presently producing ingots of stainless, high-carbon, high-speed, and structural steels. This plant is capable of producing ingots weighing up to 13 tons with a maximum cross section of 64 by 103 cm. Such plants as these continue to make the Soviet Union the largest producer of electroslag ingots in the world.

UNITED KINGDOM

Early Soviet experiences with electroslag welding and remelting encouraged British workers at Hadfields, Ltd., in Sheffield to evaluate the process on a small scale (37). Mild steel ingots from 2 to 5 cm in diameter were prepared using ac power and a 20CaF₂–15CaO–15MgO–20Al₂O₃–20SiO₂–10MnO flux. Improvements in the electrode feed mechanism permitted successful experiments on 10 varieties of steel.

In 1961, a small pilot plant for preparing 7.5-cm-diameter ingots was constructed at the British Iron and Steel Research Association (BISRA). Three years later, a larger plant with a capacity of 45-kg ingots was built (5). Independently, Firth Brown, Ltd., in Sheffield constructed the first commercial plant in Great Britain that same year. This contained a modified dc vacuum-arc furnace capable of melting ingots up to 65 cm in diameter and weighing 7 tons with 50-hertz ac power.

After several years of independent development work beginning about 1962 and of work in cooperation with BISRA, AEI-Birlec (now Birlec, Ltd.) began manufacturing commercial electroslag plants. The first Birlec three-phase produc-

¹ The term "ton" throughout this Bulletin refers to metric tons.

tion unit was installed at Henry Wiggin and Co. (5). Birlec's representative in North America is Lindberg Hevi-Duty Melting, Inc.

In 1966, an independent unit was established by BISRA (later in the British Steel Corp.) to promote the development of electroslag technology. This unit was called Electro-Slag Refining Technology (ESRT). Its duties included contract melting, evaluation trials, flux investigations, general consulting, and authorizing the licensing of worldwide plant manufacturers. One of these manufacturers was Consarc Corp. in the United States, which was among the first in America to install a commercial electroslag unit (Vasco-Teledyne-1966). Consarc has since installed a number of electroslag furnaces in the United States (table 2). Other ESRT licensees included Birlec, Ltd., GWB Furnaces, Ltd. The Rubery Owen Organization Welding Division, and Metaelectric Furnace, Ltd. Numerous British electroslag developments, some of which are outlined in chapter 16, are the result of ESRT research. In 1970, ESRT's arrangements with all manufacturers except Consarc were terminated, and efforts were redirected toward servicing the British Steel Corp. Recently, according to G. Hoyle, head of the Electroslag Development Unit of the British Steel Corp., ESRT became the Electro-Slag Development Unit of the Corporate Laboratories of the British Steel Corp.

The years 1966-67 saw the greatest increase in commercial British electroslag facilities, as can be seen in table 4. Today, Great Britain leads Western Europe in the production of electroslag-melted ingots.

AUSTRIA

Historical development of the electroslag process in Austria is essentially that of Gebr. Böhler and Co., A.G., in Kapfenberg. Böhler began investigating the process in 1962 and in 1964 constructed a pilot plant capable of ac melting ingots in a movable mold up to 30 cm in diameter and weighing 0.7 ton. By 1967, over 200 specialty steel ingots had been electroslag-melted in this plant with considerable success (8). In July 1967, commercial production of ingots up to ~80 cm in diameter (or equivalent shapes) began in a new furnace with single-phase ac power at Kapfenberg. This furnace was also equipped with a movable mold. Several nonconsumable dc electrodes surrounded the central changeable consumable electrode. These peripheral electrodes maintained a molten flux bath during melting

and when the central electrode was replaced (26). Their contribution to improved refining has also been documented (9). Later, this furnace was enlarged to produce ~100-cm-diameter ingots weighing 23 tons. In 1969, a second 56-cm-diameter unit was placed in operation, according to W. Holzgruber of INTECO, Austria.

In 1968, the Dravo Corp. in Pittsburgh became the exclusive licensee in North America for the Böhler electroslag process. Two-station ac furnaces were also being constructed in Kapfenberg and Düsseldorf in 1968 with ingot size capabilities of 55 cm and 50 cm diameter, respectively. These furnaces began production of stainless, tool, and low-alloy high-strength steels in 1969-70. One vacuum-arc furnace in Düsseldorf had previously been used for electroslag melting studies.

Present areas of development at Böhler include the production of hollow electroslag-remelted ingots and high-nitrogen austenitic and Cr-Mn steels. In 1971, an electroslag furnace capable of melting ingots up to 50 cm in diameter and 1.5 tons under 25 atm pressure was placed in operation for alloys containing elements with high vapor pressures, such as nitrogen (23). Improved mechanical properties were claimed. In 1971, Böhler completed the construction of an electroslag remelting plant for Krupp in Essen, Germany. Ingots up to 28 tons and 112 cm in diameter can be remelted in the movable-mold furnace, which has electrode-changing capabilities (19).

FRANCE

In 1963, two French companies, Compagnie des Ateliers et Forges de la Loire (CAFL, now a part of Creusot-Loire) and Compagnie Electro-Mécanique (CEM), acquired licenses for the electroslag process from V/O Licensintorg in the U.S.S.R. Subsequently, a Soviet R-951 furnace (table 3) was constructed by CEM and installed at the Ondaine works of CAFL in Firminy. Operations began in 1965 with the melting of high-speed tool steels and Cr-Ni-Mo austenitic steels. By 1967, over 40 grades of specialty steels, as well as nickel- and cobalt-base superalloys, had been electroslag-melted (1). Later, emphasis was placed on structural steels, particularly for use in the Concorde supersonic passenger aircraft. A larger electroslag furnace, capable of melting ingots up to 4.5 tons and 65 cm in diameter, was built later in Firminy (26). Several additional Soviet licenses were granted to CAFL and CEM for bifilar furnaces and siphon-slag starting as described in

Table 4.—Commercial electroslag meeting facilities in the United Kingdom

Company	Location	Number and type of furnace(s)	Maximum ingot—		Power ¹	Year startup	Metals produced	Estimated annual capacity, net metric tons	References
			Diam., cm	Weight, kg					
Edgar Allen Steel.	Sheffield	1—Birlec	38	1,090	ac	1968	Various steels.	1,500	22, 41
J. Beardshaw and Sons, Ltd.	Sheep-bridge.	----- do -----	23	NA	ac	1966	Tool and stainless steels.	NA	22, 26, 30, 41
Brown Bayley Steels, Ltd.	Sheffield	----- do -----	28	680	ac	1967	Alloy and high-speed steels.	1,000	22, 41
R. W. Carr	----- do -----	3—Birlec	23	2,700	ac	1968	High-speed and hot die steels.	4,500	22, 41
Firth-Brown, Ltd.	----- do -----	1—own design	64	2,700	ac ²	1964	High-tensile and stainless steels.	2,000	26, 30, 41
Do	----- do -----	1—Birlec	61	NA	ac	1973	----- do -----	NA	17
Do	River Don Works.	1—formerly British Steel Corp.	50	1,800	ac	1967	Specialty steels.	NA	26, 31, 41
			90	13,600	ac ²				
J. Gillott & Sons, Ltd.	Sheffield	1—Rubery-Owen.	25	NA	ac	1966	Tool and die steels.	670	26, 30, 41
Hall and Pickles, Ltd.	Man-Chester.	1—Birlec	23	450	ac	1966	Tool steels, Ni—Cr alloys.	800	26, 30, 41
Jones & Colver	Sheffield	----- do -----	30	680	ac	1967	Tool steels	1,100	26, 30, 41
Kayser Ellison.	----- do -----	----- do -----	25 (square)	NA	ac	1967	Alloy steels	4,500	22, 41
			28	3,600	ac ²				
Samuel Osborn & Co., Ltd.	----- do -----	----- do -----	86	NA	ac	1967	----- do -----	6,000	25, 26, 41
			36	3,600	ac ²				
Wm. Oxley & Co.	Rotherham	1—GWB furnace	91	NA	(³)	1972	Stainless steels, Nickel-base alloys.	4,500	26, 41
Sanderson-Kayser, Ltd.	Darnall	1—Birlec	115	NA	ac	1967	Alloy steels	4,200	25, 26, 41
Union Carbide UK, Ltd.	Glossop	1—Birlec	30	2,700	ac ²	1970	Nickel- and cobalt-base alloys.	5,300	Hoyle ⁴
			91	4,000	ac				
Henry Wiggin and Co.	Hereford	----- do -----	91	6,400	ac ²	1967	Nickel-base alloys.	6,800	Hoyle ⁴
			40	NA	ac			30	
		----- do -----	122	4,000	ac ²	1970	----- do -----	25,000	41
			63.5	4,500	ac				
			107	15,000	ac ²				

NA Not available.

¹ All single-phase ac unless otherwise indicated by footnote.² 3-phase ac.³ Both single-phase and 3-phase.⁴ Personal communication, from G. Hoyle, 1972, available for consultation at Bureau of Mines, Albany Metallurgy Research Center, Albany, Oreg.

chapter 17. CEM is also licensed to sell Soviet-designed furnaces throughout Western Europe.

In 1970, it was reported (15) that Commentre des Aciers Fins Vanadium Alloys had contracted Heurtey, Ltd., for the construction of an electroslag remelting plant featuring a 46-cm-diameter, 6-ton movable-mold furnace. This furnace was placed in operation in 1971, according to W. Holzgruber. Heurtey is a licensee of the Böhler process. Four 6- to 10-ton electroslag remelting furnaces were also reported to be under construction at Usines de la Loire de CAFL in 1970 (15). However, no further reports concerning these furnaces have been noted.

FEDERAL REPUBLIC OF GERMANY

Heraeus Hochvakuum G.m.b.H. in Hanau (now Leybold-Heraeus), as well-known manu-

facturer of vacuum furnaces, began experimenting with electroslag melting parameters in cooperation with Firth Sterling prior to 1967.

In 1965, Rheinstahl Hüttenwerke A.G. in Hattingen installed a single-phase ac electroslag pilot plant of their own design, capable of melting specialty steel ingots up to 30 cm in diameter (43). This was followed in 1968 by a developmental three-phase ac furnace with steel molds which could either simultaneously melt three ingots up to 60 cm in diameter weighing 2.8 tons, or melt one ingot up to 130 cm in diameter weighing 11 tons from three electrodes (43).

In 1968, Stahlwerke Südwestfalen installed the first commercial electroslag plant in Germany. This consisted of three ac furnaces manufactured by Otto Junker, G.m.b.H., a licensee of Birlec,

Ltd., in the United Kingdom. Ingots up to 125 cm in diameter could be electroslag-remelted.

Several additional electroslag plants have since been completed in Germany. Among these is a single-phase ac furnace of Heraeus design which went into operation at Edelstahlwerke Witten, A.G., in 1969 and is capable of melting 70-cm-diameter ingots. A single-phase ac 4-ton electroslag furnace was completed in 1970 for Deutsche Edelstahlwerke A.G. in Krefeld. In addition, one 7.5-ton vacuum-arc dc furnace was modified for electroslag melting 50-cm-diameter ingots. Stainless steels and high-temperature alloys are the major electroslag products (32). In 1971, a 220-ton Leybold-Heraeus ac-dc electroslag remelting unit was completed at Stahlwerke Röchling-Burbach G.m.b.H. in Völklingen. Maximum ingot size is 270 cm in diameter (7). A new variety of electroslag furnace has recently been offered by Leybold-Heraeus (21).

SWEDEN

The electroslag process found acceptability in Sweden somewhat later than in other industrialized countries. However, there has been a flurry of activity in the past 3 years.

Fagersta Bruks A.B. (now Fagersta A.B.) has had a Rubery Owen furnace capable of producing 25-cm-square ingots in operation since the 1960's. Two new 50-cm-diameter electroslag furnaces were scheduled to be operational in 1972 (16). Suruhammars Bruks A.B. has a 70-cm-diameter Rubery Owen furnace which was completed in 1969. Uddeholm installed an ac Böhler-type plant in Hagfors in 1970 for melting 27-ton ingots up to 102 cm in diameter of tool and structural steels. That same year, Soderfors Bruk commenced operation of a Birlec electroslag furnace with a 90-cm-square maximum ingot size. A.B. Bofors was also reported to have an electroslag refining plant with two Böhler furnaces (50 and 100 cm in diameter, 10- and 27-ton capacity) completed in 1970 (15).

In 1969, Avesta Jernverks A.B. purchased a Soviet license for a U-436 ac double-electrode bifilar furnace and a siphon flux-pouring mechanism. Full-scale production of stainless steel slabs weighing up to 9 tons began in 1971. Annual capacity is estimated at 5,000 to 6,000 tons. A new 61-cm-diameter, 10-ton Böhler furnace is scheduled for startup in 1973 at Uddeholm, according to W. Holzgruber.

ITALY

Italy's Cogne has had electroslag remelting capabilities since before 1969. Three Birlec units capable of operating on single-phase ac (40-cm-diameter maximum ingot size) and three-phase ac (120-cm-diameter maximum ingot size) comprise their equipment. A new 102-cm-diameter, 24-ton Böhler furnace is scheduled to be placed in operation at Tassara in 1973, according to W. Holzgruber.

BELGIUM-LUXEMBOURG

Considerable developmental electroslag work involving the Arcos process (see chapter 17) and direct melting of prerduced iron ore pellets has been conducted in Belgium over the past few years. Two Böhler furnaces, each with a capacity of 102-cm-diameter ingots of 27 tons, were to be completed at Cockrill-Ougree, Belgium in 1973, according to W. Holzgruber. It has been reported that electroslag remelting equipment was installed for ARBED in Luxembourg in 1971 (17).

ISRAEL

Alloymet Israel Ltd., a subsidiary of Alloy Metal Products, Inc., has established a pilot plant to produce electroslag-melted high-speed steels. The plant is located in Natanya and consists of one Birlec 180-kva furnace, according to R. C. Simpson, Alloy Metal Products, Davenport, Iowa.

JAPAN

Soviet electroslag research enabled Japan Special Steel Co., Hitachi Metal Industry, Ltd., and Kobe Steel, Ltd., to further develop the process as early as 1962. In 1967 it was reported (24) that Japan Steel was electroslag-melting high-speed steel ingots in sizes up to 16 cm in diameter and weighing 1 ton; Hitachi was making ingots in sizes up to 28 cm in diameter, and Kobe was making ingots up to 48 cm in diameter. In 1968, Japan Steel began operations with a single-phase ac 4-ton furnace. Kobe Steel began negotiating with the U.S.S.R. in 1965 to obtain a license and manufacturing rights to construct an electroslag plant. At its Takasago works, one furnace capable of melting specialty steel ingots up to 80 cm in diameter is in operation.

Since 1966, Mitsubishi Heavy Industries has also been involved in electroslag remelting specialty steels and superalloys.

A new 75-ton Paton electroslag furnace is expected to be operational in Japan in the near future for refining Marine steels (18). In addi-

tion, Daido Steel Co., Ltd., completed construction of a 2-ton electroslag remelting furnace in 1971. It has also been reported that Mitsui has signed a licensing agreement with the Soviet Union for two electroslag furnaces. According to a recent report, Japan had 23 electroslag furnaces with capacities greater than 100 kg in operation by the end of 1972, with 2 under construction (6).

OTHER COUNTRIES

Laboratory-scale experiments in India have led to the installation of a Soviet R-951 furnace.

An electroslag pilot plant has been operating in Czechoslovakia since 1961. Considerable research has been conducted in evaluating the mechanical properties of electroslag-remelted ball-bearing steels in that country.

In East Germany, a 1-ton electroslag furnace has been in operation for several years at the Edeltahlwerke plant in Freitel.

In Poland, two 2-ton Soviet R-951 electroslag furnaces are operating. Electroslag installations have also been reported in Hungary, Romania (26), and Yugoslavia (44).

Recently, it was reported (20) that a Consarc electroslag furnace capable of producing ingots up to 81 cm in diameter and slabs measuring 46 by 91 by 229 cm will be installed near Sao Paulo, Brazil. Tool, high-speed bearing, and stainless steels will be produced.

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CHAPTER 2.—ELECTROCHEMICAL REACTIONS IN THE ELECTROSLAG PROCESS

By A. Mitchell ¹

Many steelmakers would wish to use the electroslag process simply as a remelting method to improve ingot structure. However, it has been observed on innumerable occasions that the metal undergoes chemical changes when it is processed by the electroslag method. In some cases (for example, that of low sulfur contents) the changes may be useful, but in others (for example, oxidative loss of reactive alloy elements) the changes may be a major disadvantage. Evidently, in such a situation we must endeavor to explain and control pertinent reactions, and to exploit the system's characteristics to metallurgical advantage. Let us examine first the general scheme of reactions which have been observed in the process.

GENERAL OBSERVATIONS ON REACTIONS

The most common observation that has been made on electroslag process reactions is that there is a considerable difference in metal composition depending on whether direct or alternating power is used. Although in most instances conditions were not accurately comparable between the power modes (with respect to melt rate, for example), the observation is sufficiently general to warrant the conclusion of a real difference due to power mode.

It is a second generally accepted conclusion that the operative reaction scheme in both ac and dc power is a function of flux composition. As an example of this, we may quote the observation that desulfurization is a function of basicity (1). Again, however, generalizations are potentially misleading since the temperature-mass flow regime does not remain constant as a function of various flux compositions.

Our final general observation on reactions is that we must always account for the presence of

air above the process. For example, sulfur can be lost through the gas phase by oxidation. Very little melting has been carried out in an inert atmosphere, and consequently, we have very steep gradients in oxygen potential in the high-temperature regions.

REACTION SCHEMES

The Electroslag Furnace as a Single-Stage Reactor

Since in an electroslag furnace, we progressively melt an electrode through a single, fixed volume of flux, it is tempting to treat the system as a single-stage reactor. Several workers (4-6) have applied such a treatment to chemical changes occurring in the process, using development of the basic equation

$$\ln \left(1 - \frac{[X]}{[X_0]} \right) = - \text{constant} \cdot W_m \quad (1)$$

where $[X_0]$ and $[X]$ are the electrode and ingot concentration of X, respectively, and W_m is the ratio of metal-to-flux weight at the time when $[X]$ describes the ingot concentration of X. The constant includes terms such as equilibrium constants, activity coefficients, etc.

This equation assumes thermochemical equilibrium and has not been applied successfully to a real system. A modification of the equation, to allow for nonequilibrium, was used by Etienne and Mitchell (2) to describe changes in composition due to oxidation during remelting. These workers found that the relationship fitted results during 60-hertz ac melting with a reasonable value for the mass-transfer coefficient. However, this latter value had no theoretical derivation. Furthermore, on applying the model to a direct current process, no realistic fit could be obtained. The changes in composition observed were essentially independent of the parameter W_m as shown in figure 6 and could not be rationalized in terms of the single-stage reactor model. It was suggested that electrochemical reactions provided

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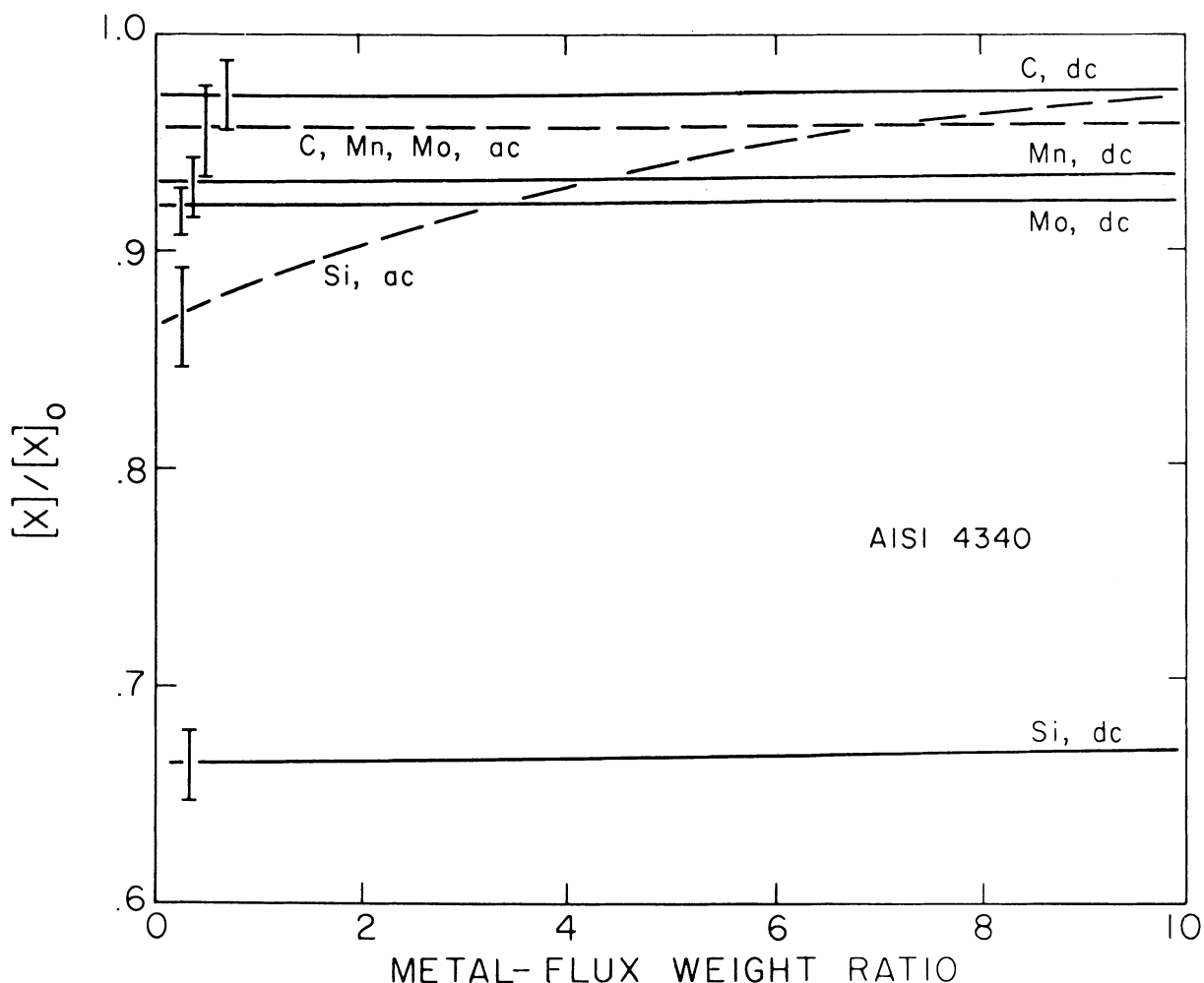


Figure 6.—Changes in metal composition due to electroslag melting in CaF_2 -25 wt-pct Al_2O_3 under an inert atmosphere (2). The arrows denote $\pm 2\sigma$.

local subsystems which could only be modeled using the scheme which allowed for three distinct and independent mass transfer sites: electrode-flux, droplet-flux, and ingot-flux interfaces.

Separation Into Three Reaction Sites

The three individual sites at which either chemical or electrolytic reactions may take place can be reasonably well defined from a mass-transfer viewpoint. A conical electrode tip with a film of metal moving down its surface has a characteristic metal residence time. In addition, by making assumptions as to the local hydrodynamic conditions in the flux, we may derive an expression for mass-transfer rate. In this, we must allow for local equilibrium at the flux-

metal interface, but we may have diffusive control in either or both phases. In a similar fashion, we may also treat the falling drop as a separate reaction system which commences with the product of the electrode-flux reaction. Finally, we may derive a mass-transfer expression for the ingot-flux interface using the same assumptions as in the case of the electrode-flux site. The sum of these three reactions should be equal to the overall observable reaction rate in the process. A preliminary treatment of this sequence has been made (3) and found to account well for chemical changes in 60-hertz, inert atmosphere melting. However, the special conditions outlined below of direct current melting have so far proved intractable.

ELECTROCHEMICAL REACTIONS

In principle, at the site of a Faradaic reaction we may expect to find polarization from a number of causes. At low temperatures, particularly when solid phases are involved, thermally activated reaction steps can give rise to significant potential gradients. However, in high-temperature systems, this situation has only rarely been observed. The anode phenomena at graphite-cryolite electrodes are probably the best known example of this. In the electroslog case, we are dealing with very high temperatures and a liquid electrode-liquid electrolyte interface. As would be expected, experimental work (12) has shown that the polarization observable at such interfaces is entirely due to concentration effects. To understand these effects, it is necessary to examine, first of all, the direct current case. After this, we will transpose this situation to that of line-frequency single-phase ac melting.

Direct Current Polarization

The necessary experimental work to establish the nature of direct current polarization was done by Mitchell and Beynon (11), who examined the polarization at iron-flux interfaces for a range of CaF_2 -based slags. Essentially the method consisted of applying a galvanostatic pulse to a melting iron electrode and making an oscillographic measurement of the resulting polarization. The cathode reaction produced very small polarization potentials, indicating a rapid diffusion to the interface, as would be expected in a system with effectively infinite cation concentration. The anodic process, on the other hand, gave a three-stage sequence of polarization behavior as the current density was increased. An example of this is shown in figure 7, for one of the fluxes studied. The first two stages are of most importance for practical purposes. The first of these (I of figure 7) was postulated to result from the corrosion reaction;



which would lead to polarization potentials tending to infinity as a limiting current density was reached. The current density at which such a situation would appear was found to be higher than that at which a new form of reaction appeared (II of figure 7), where the polarization potential was essentially independent of current density. This was explained by means of the phase relations in the system $\text{CaF}_2 + \text{Al}_2\text{O}_3 + \text{FeO}$ (or $\text{CaF} + \text{CaO} + \text{FeO}$), whereby a second liquid-phase rich in FeO is precipitated as the

Fe^{2+} concentration is increased (7). Thus, as the corrosion reaction proceeds, an FeO-saturated layer appears at the iron surface and holds the polarization potential constant. With increased current density, the layer thickens but retains the Fe-FeO potential at a constant value. No evidence was found for the direct disposition of any anion.

We can now see that an interesting situation arises when an alloy is exposed to such an anodic reaction. In the case of chromium, vanadium, nickel, or cobalt, exactly the same behavior is observed as is the case for iron. This is shown in figure 8. However, the "plateau" potentials differ, reflecting the differing stabilities of the metal-metal oxide couples produced at saturation. When we anodically polarize an alloy of Fe-Cr we would expect therefore to produce Cr^{3+} in preference to Fe^{2+} . This is indeed the case, as is seen from curve A in figure 9. When the current is applied for a significant length of time ($i_0 \cdot t > 2$ coulombs), the metal surface becomes depleted in chromium and iron is corroded in its place. Hence, we observe curve B of figure 9, and a corresponding chromium gradient in the quenched electrode surface (fig. 10). The important conclusions of these experiments are that anodic reactions cannot take place at significant rates in steels under anodic potentials exceeding that of Fe- Fe^{2+} , and that surface depletion will occur by anodic corrosion.

From these conclusions we can eliminate much of the speculation which has surrounded electrochemical reactions in electroslog melting. We may say with certainty that direct anodic processes such as



do not occur on iron surfaces. We may also say that oxidation must take place by secondary reaction with the Fe^{2+} produced at the anode.

The relation of reactions 3-6 to electroslog processing is now clear. At the anodic surface, we produce a high concentration of Fe^{2+} , leading in the limit to separation of a discrete layer saturated in FeO. At the cathode, we will discharge either Ca^{2+} or Al^{3+} , or both, depending on the flux composition. This explains the small increases of Ca and Al_2O_3 -type inclusions occasionally observed in electroslog-melted ingots. The reaction system, therefore, consists of three

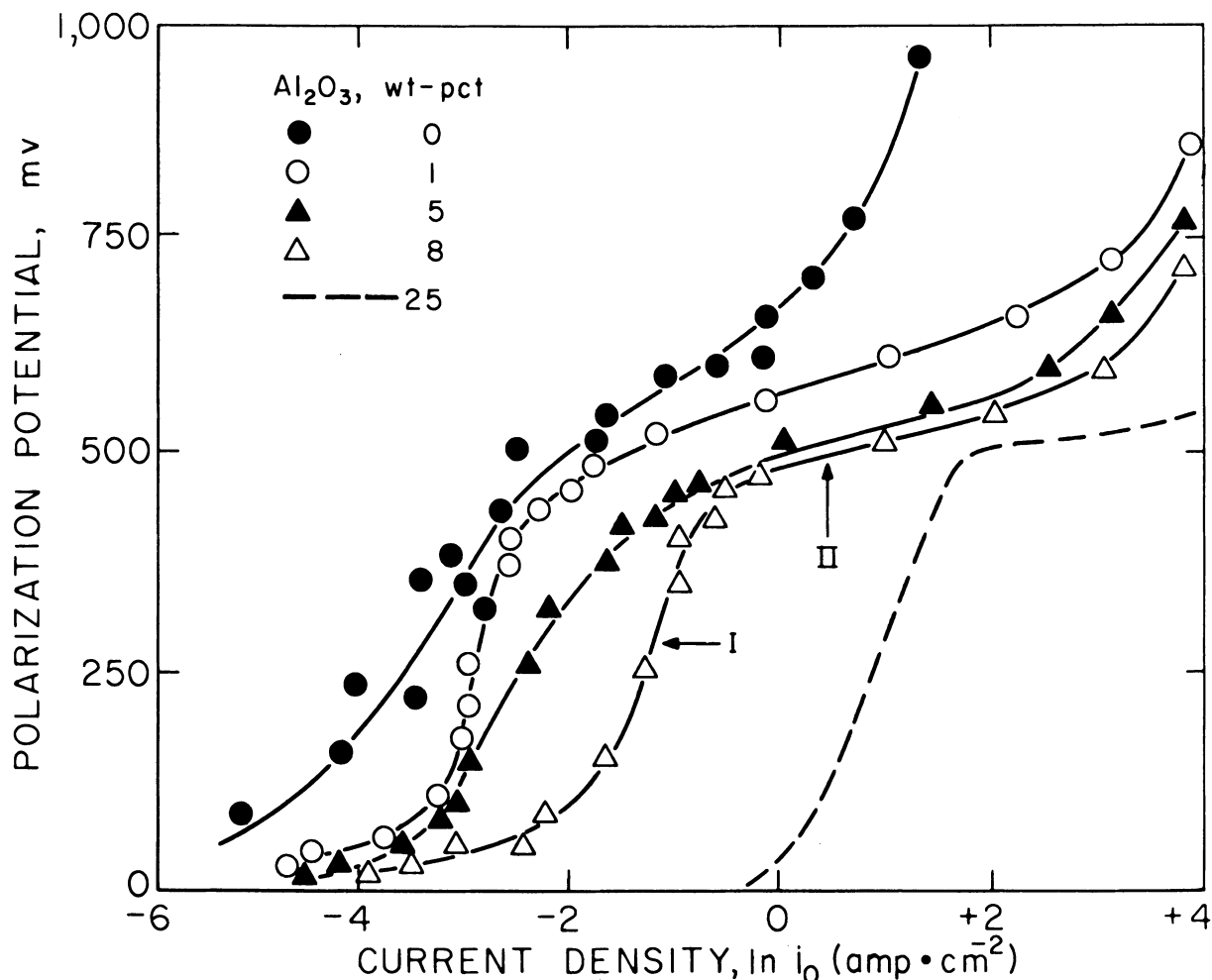


Figure 7.—Anodic polarization behavior of an iron surface subjected to galvanostatic anodic pulses during electroslag melting with a $\text{CaF}_2\text{-Al}_2\text{O}_3$ flux.

distinct sites: the two electroactive surfaces and the nonelectroactive droplets. We shall now examine this proposal in the light of known chemical changes in direct current melting.

Direct Current Melting

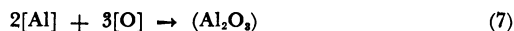
Oxidative losses of alloy elements occur during direct current melting, whether the consumable electrode is the positive or the negative pole.

The losses may be very large, as in the case of titanium and aluminum in nickel- and iron-base alloys with the electrode negative, or they may be small, as in the case of manganese and silicon from steels. The losses are proportionately smaller in large ingots than in small ones, and are approximately independent of the amount

of metal which has been melted through the flux volume. We may rationalize all these observations in the light of the polarization described above.

The three reaction sites are distinguished in direct current melting as shown in figure 11.

The reaction



applies to the case of aluminum in solution with iron, together with oxygen (11). For this case, we will follow the reaction scheme shown in figure 12. Hence, we will arrive at an ingot composition which has two important features: the aluminum and oxygen contents are not in the stoichiometric ratio of Al_2O_3 , and the behavior

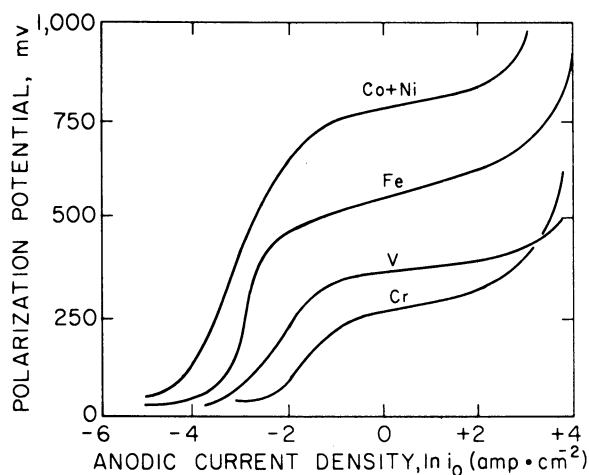


Figure 8.—Anodic polarization behavior of Co, Ni, V, Cr, and Fe surfaces subjected to galvanostatic anodic pulses in a CaF_2 -1 wt-pct Al_2O_3 flux. The curves for cobalt and nickel are identical.

of the aluminum and oxygen contents on remelting will be influenced by the Al_2O_3 activity in the flux, but cannot be related to this latter quantity in any precise way.

The first feature arises because there is no restriction on the aluminum-oxygen ratio in the separate electrolytic sites, as there would be if the aluminum and oxygen content arose by simple equilibration with Al_2O_3 . The second feature

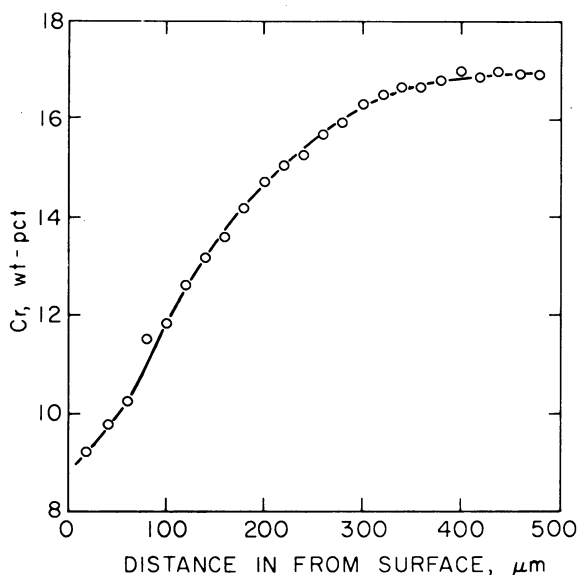


Figure 10.—Chromium depletion in the electrode surface quenched from point C of figure 9.

is found since the droplet contribution is a finite, but small part of the overall scheme.

Similar reactions can be proposed for other situations involving metal-metal oxide equilibria. The extent of these reactions will depend on (1) the current density, (2) the flux composition and metal composition, and (3) the specific metal residence time at each site. The current density enters the picture in two ways. First, the combination of current density and metal residence

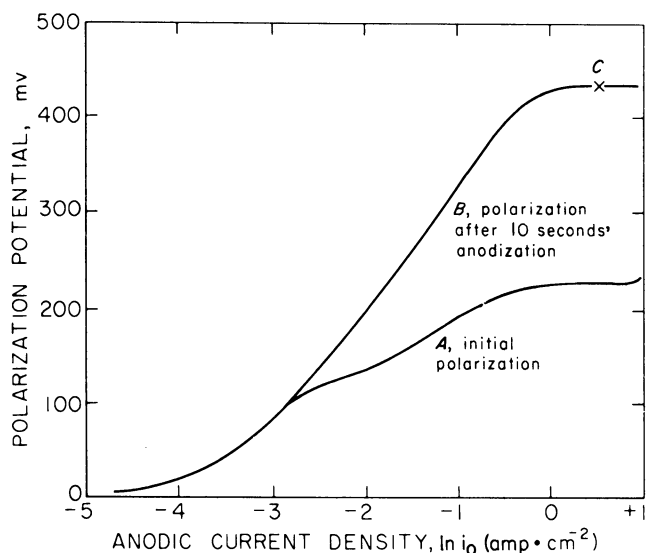


Figure 9.—Polarization of anodic Fe-17 wt-pct Cr surface, showing effect of Cr depletion in the metal at the flux-metal interface.

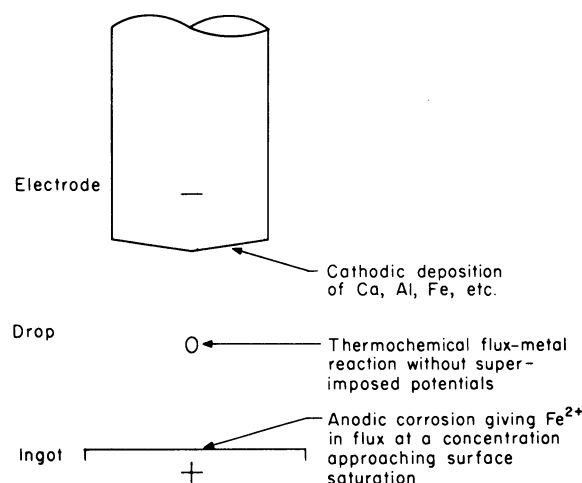


Figure 11.—Schematic diagram of a direct current electroslag melting regime.

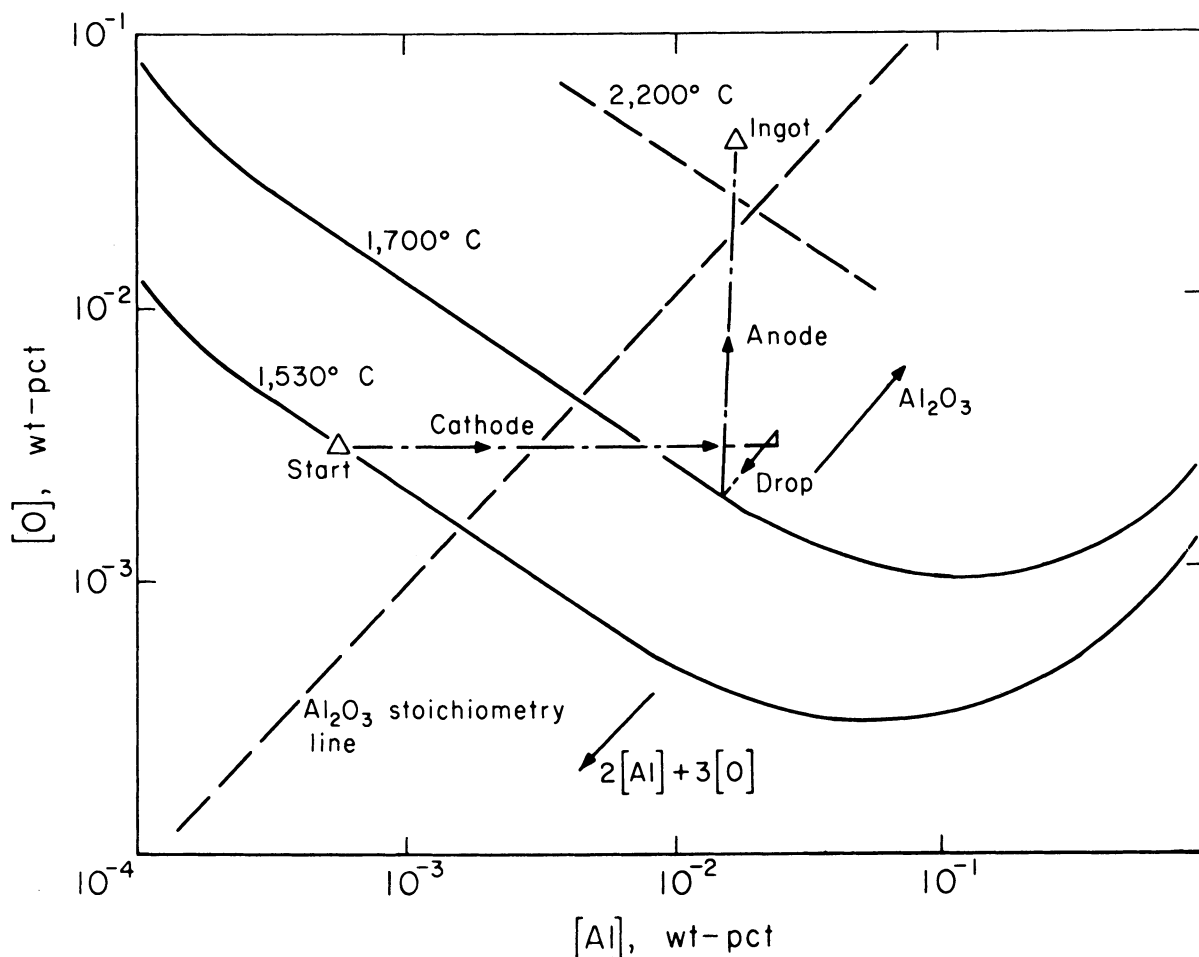


Figure 12.—Schematic diagram for the equilibrium reaction



showing the postulated reaction path for a direct current melt of pure iron with the electrode as the negative pole (dot-dashed line).

time determines the theoretical extent to which Faradaic reaction can achieve composition change. Second, the current efficiency is a function of current density. In the special case of our corrosion reaction to produce Fe^{2+} , once the "saturated layer" condition has been reached, further increase in current density will not produce a higher oxygen potential. We would expect then that this reaction site will have a maximum limiting rate at this condition.

The flux and metal compositions are part of the reaction scheme as described above. The reactions are diffusion controlled in either or both phases, and so the concentration of the diffusing elements influences the rate of reaction. In addition to this effect, there is a second condition,

again related to the formation of the Fe^{2+} saturated layer. There are flux compositions in which this will occur at extremely low Fe^{2+} concentrations (12). Therefore, we expect to see enhanced anodic oxidation rates in such fluxes. The influence of the specific metal residence time is obvious. At high metal-throughput rates, a given rate of oxidation will produce smaller net composition changes than would a small throughput rate.

The system polarity influences the reaction scheme primarily through current density. The electrode and ingot have differing areas, giving the electrode a higher current density. If both

the electrode and ingot have a current density high enough to saturate an anodic surface in Fe^{2+} , we would expect little influence of polarity on oxidative losses. However, in most instances this is not the case, and the high-current-density site at the anode will produce the highest oxidation rate. The oxidation rate is not to be confused with ingot oxygen content in this context.

In summary, direct current melting is primarily controlled by reactions at the two electrochemically active sites, and only slightly influenced by thermochemical equilibration at the droplet-flux site.

Alternating Current Polarization

Due to the experimental difficulties involved, there is much less known about alternating current polarization at high temperatures than about the equivalent direct current reactions. There are, however, some connecting features in the two cases. At high temperatures, diffusion is extremely rapid, and the time required for the establishment or destruction of a concentration gradient is very short. If we examine the transition between direct and alternating current polarization, this feature becomes evident. In figure 13, we show the polarization effect of successive fast galvanostatic pulses of direct current applied anodically to an iron-flux interface. The Fe^{2+} produced in the n th pulse contributes to the polarization found in the $(n + 1)$ th pulse, eventually resulting in the establishment of an Fe^{2+} -saturated layer. We would expect from this result that a steady state would be reached where the pulse production of Fe^{2+} was balanced against

hydrodynamic and diffusive losses from the local system. As a second pertinent experimental observation, in the case of isolated, but fast, galvanostatic anodic pulses, we find that

$$i_o t = \text{constant} \sim 2 \text{ coulombs}, \quad (8)$$

$$i_o = \text{current density},$$

$$t = \text{time to reach the plateau potential of figure 7 at } \text{Fe}^{2+} \text{ saturation.}$$

This relation is found to apply down to times of the order of 1 msec. We may conclude from the above observations that the general form of the cathodic and anodic reactions will remain the same, even at polarization times equivalent to 60-hertz half-cycle periods. The most fundamental difference between 60-hertz and direct current polarization is that the result of one half-cycle is present at the initial application of the next half-cycle in 60 hertz. We may, therefore, envisage the following scheme: the electrode corrodes anodically, giving Fe^{2+} , and the same Fe^{2+} is deposited cathodically, in preference to the Ca^{2+} and Al^{3+} ions in the flux. As this scheme stands, there is no net change in the electrode composition. We have assumed, however, that the cyclic process is completely reversible, which is not necessarily the case. We can suggest a modification to the scheme in which we take into account the concurrent convective and diffusive loss of Fe^{2+} to the system. This scheme is illustrated in figure 14, where the Fe^{2+} loss must be compensated for by a Ca^{2+} -Ca reaction (or an Al^{3+} -Al reaction). Attempts to model this process have so far produced inconclusive results. In theory, it should be possible to detect the nonreversibility by a close examination of the waveform in 60-hertz melting. Unfortunately, the small change we expect to find (about 500 mv in a 100-volt peak-to-peak signal) is completely overwhelmed by the normal deflections in waveform caused by system reactances. Since the Fe^{2+} loss corresponds to a net rectification of the 60-hertz signal, we should also be able to detect an equivalent direct current component. Again, due to the very small size of this component, experiments have as yet produced no definitive result. This somewhat conjectural picture has produced one positive result: We may say with a degree of certainty that current transfer at 60-hertz is Faradaic, almost entirely reversible, and due to the fast exchange of Fe and Fe^{2+} . We may neglect, for most practical purposes, the very small rectification effect, and also current transfer by capacitive means.

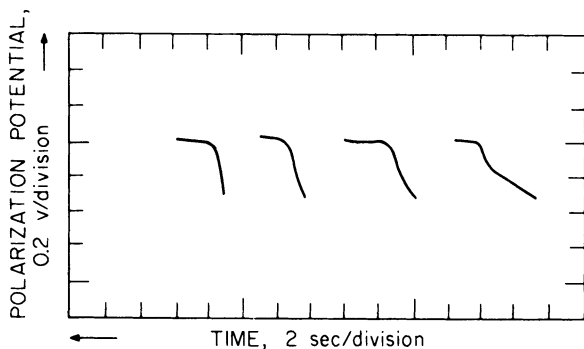


Figure 13.—Successive anodic polarization pulses at $1 \text{ A}\cdot\text{cm}^{-2}$ on a pure iron electrode in a CaF_2 -1 wt-pct Al_2O_3 flux. The progressive development of the "plateau" potential can be clearly seen.

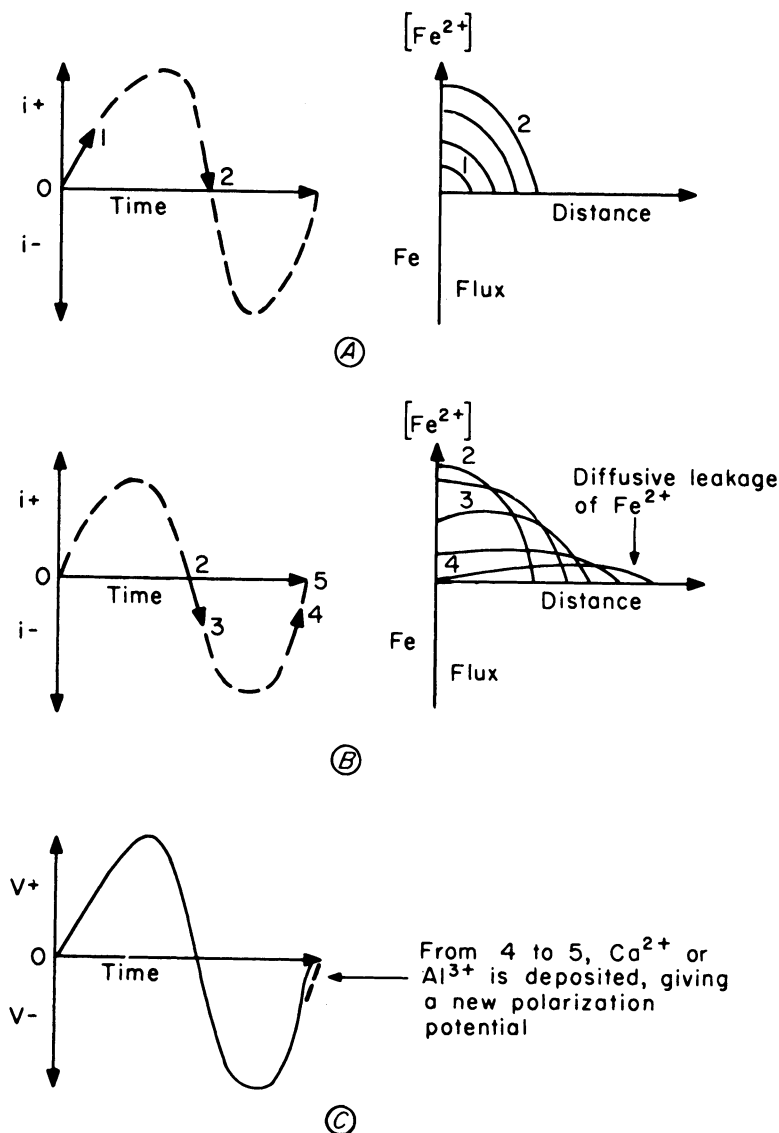


Figure 14.—Schematic diagrams of alternating current polarization at an iron-flux interface: *A*, The anodic pulse produces a concentration gradient of Fe^{2+} in the flux; *B*, The cathodic pulse destroys the Fe^{2+} gradient close to the surface, but Fe^{2+} continues to diffuse out into the flux under the existing concentration gradient; *C*, The cathodic pulse shows a change from $Fe-Fe^{2+}$ to $Fe-Al^{3+}$ or $Fe-Ca^{2+}$ at the point when the interfacial concentration of Fe^{2+} reaches zero.

Line-Frequency (ac) Melting

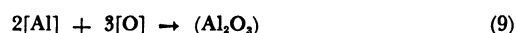
Although in 60-hertz melting, we have the same three reaction sites as obtained in the direct current process, the net reactions will be quite different. The electroactive sites are effectively "blocked" to reactions above the $Fe-Fe^{2+}$

corrosion potential, and those occurring below this (for example, $[Cr] \rightarrow (Cr^{3+}) + 3e^-$) are depleted at the active interface. For elements in concentrations that will produce significant loss by surface depletion, the electrode and ingot sites will provide positions where electrochemical re-

action can occur. For elements in small concentration (for example, oxygen), the droplet site will be most important.

Let us now examine how the foregoing arguments can be related to practice. In the case of a minor element reaction (for example, the introduction of oxide inclusions), we have suggested that the droplet site, reacting towards thermochemical equilibrium, is the most important. We would expect to find correlations between the ingot oxygen content and the thermochemistry of oxide components in the flux. Such relationships have been observed on many occasions for FeO, Al_2O_3 , and SiO_2 in fluxes (10). Upon careful examination, however, in the few cases where flux thermodynamics are well established, we find that, although a qualitative correlation

exists for trends in oxygen content as a function of flux oxide activity, the numerical quantities involved do not agree with calculations (11). In most cases, the apparent equilibrium temperature is too high ($>2,000^\circ\text{C}$) for agreement with experimental observation (5). We would suggest that the disagreement can be due to the participation of some electrochemical reaction in the major droplet reaction. The scheme for the reaction



would then appear as shown in figure 15.

In the case of major alloy elements (for example, silicon and manganese in steels), there is sufficient alloy in the material to provide a high rate of corrosion at both the electrode and the

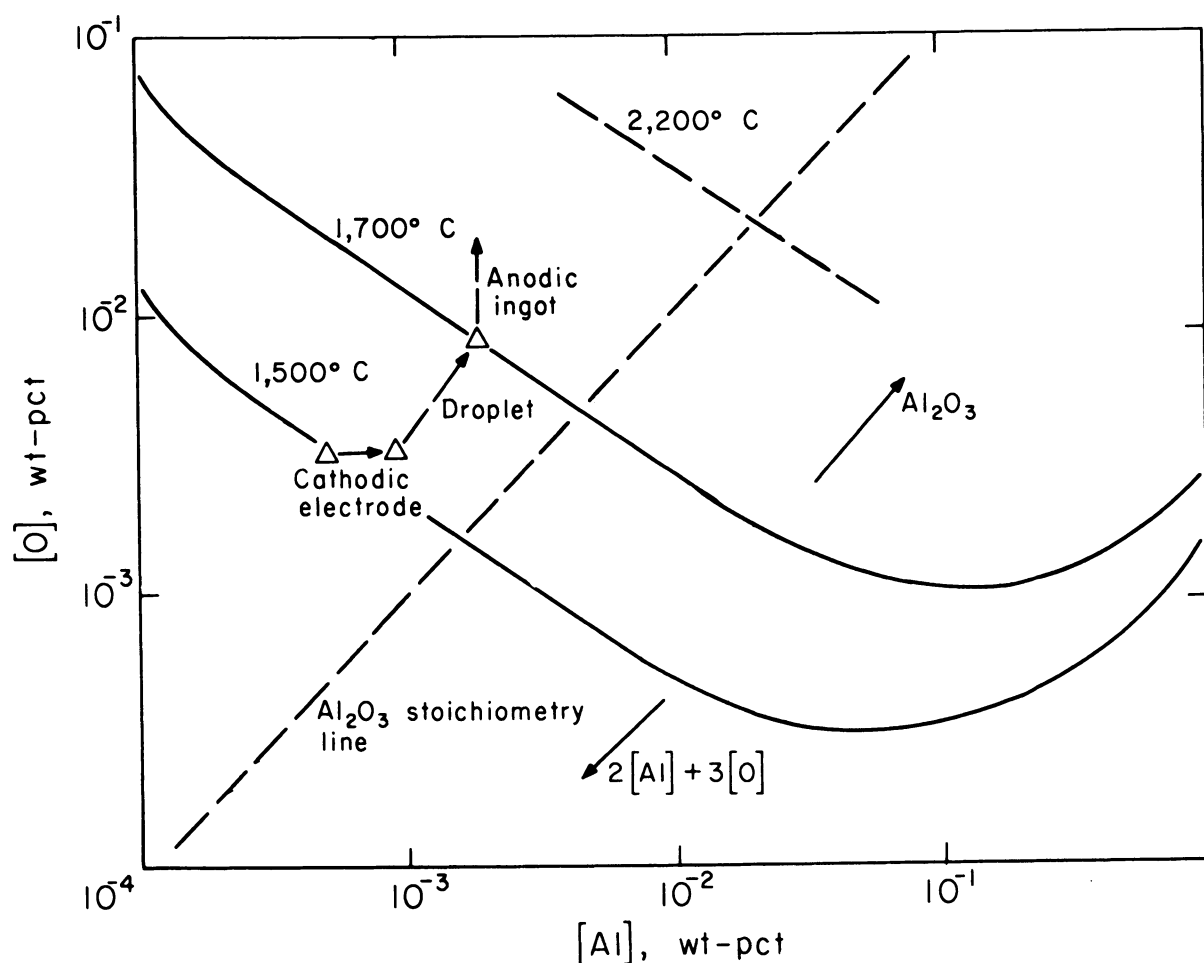
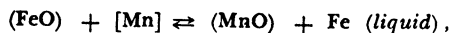


Figure 15.—Schematic diagram for the equilibrium reaction $2[\text{Al}]_{1 \text{ wt pct Fe}} + 3[\text{O}]_{1 \text{ wt pct Fe}} = \text{Al}_2\text{O}_3$ (l)(ac melting) showing the projected path (dot-dashed line) for the electroslag reactions of pure iron during ac melting.

ingot in addition to the droplet-flux reaction. If the particular reaction concerned has an equilibrium constant close to unity, for example,



the temperature difference between the electrode and the ingot may produce a situation in which material is corroded from the electrode but re-deposited from the flux at the ingot surface. It has been found by manipulating the concentrations involved in such a reaction, that there is a very significant reaction rate at the ingot-flux interface (3).

In summary, we may say that the polarization mechanisms operative at 60 hertz produce a much smaller concentration change in the process than is observed in direct current melting. The changes are characterized by small, but significant deviations from thermochemical predictions.

CONTRIBUTING REACTIONS

Atmospheric Reactions

In examining the effects of inert atmosphere electroslag melting, as opposed to air electroslag melting, one of the most noticeable features is that the direct current process electrical resistance is quite different from that of 60 hertz. The flux's apparent resistivity is approximately 60 percent of the 60-hertz value, this latter value approximating the theoretical. It is thought that this effect is due to a solution of either calcium or aluminum metal in the flux, produced electrochemically at the cathode. If the current mode is changed rapidly from dc to 60 hertz, the flux recovers its theoretical resistance in approximately 10 seconds, indicating that a physical diffusion process is required to achieve the transition. In air, this effect does not appear, because reaction at the flux-air interface continuously oxidizes the metal component.

Air-melted and inert-gas-melted direct current ingots show the same oxidative behavior. In view of the foregoing discussion which attributes chemical changes to electrochemical reactions, this finding is not surprising. In 60-hertz melting, ingots melted in an inert atmosphere uniformly show lower oxygen contents than those prepared in air. Once again, since the flux bulk composition is more important in determining the ingot composition in this case, this finding is not unexpected.

Temperature Effects

It is well established that superheating of the metal melting on the electrode tip is extremely small, possibly 5° to 20° C above the liquidus (9). Hence, we expect that the reactions occurring at this site will correspond closely to those at the liquidus temperature, which, of course, varies widely with alloy composition. The droplet is superheated from the electrode temperature to that of the ingot surface during its fall, and thus follows a temperature profile from the liquidus to approximately 1,750° C. The ingot-flux interface in the melting of steels has an average temperature of approximately 1,650° C, but rises to 1,750° C in the center. It is evident, then, that we cannot regard the system as isothermal. For some instances, as in the case of a completed reaction at the electrode, the system reduces to an isothermal situation. However, for the great majority of reactions, it is extremely important to allow for the effects of temperature variation.

Effects of Frequency

We have considered only the effects of 60 hertz in our discussion. Evidently, the degree to which frequency influences the overall electrochemistry depends on the nonreversibility of the cyclic process. As the frequency decreases, there will be proportionately more "leakage" of Fe²⁺ from the local electrochemical system. In practice, the frequency range in which a chemical effect begins to appear is 3 to 5 hertz, at which point the net rectification begins to produce effects equivalent to direct current melting, according to A. Choudhury, metallurgist with Stahlwerke Röchling-Burbach GmbH, Völklingen, West Germany.

Electrical Configuration

We have implicitly assumed in our descriptions of the process that all the process current passes through the electrode and ingot interfaces with the flux. In the so-called live mold process, this is not true, and a significant proportion of the process current does not pass through the ingot. In this event, there is very significant rectification of the mold current component with corresponding electrochemical reactions at all three sites (mold, electrode, ingot) (8). The precise nature of these reactions is at present unclear.

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² Titles enclosed in parentheses are translations from the language in which item was published.

CHAPTER 3.—THERMOCHEMISTRY OF THE ELECTROSLAG PROCESS

By R. H. Nafziger

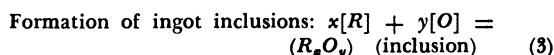
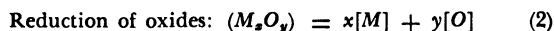
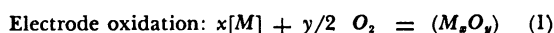
One of the advantages claimed for the electroslag process over other, more conventional secondary melting techniques is the potential refining capability of the flux. As an aid to understanding this aspect, it is necessary to consider the general thermochemistry of the process with specific reference to the behavior or partitioning of key elements between flux and metal phases. In chapter 2, it was shown that equilibrium thermochemical considerations are most pertinent to reactions which occur at the molten metal droplet-flux interface in the electroslag process. This chapter presents a brief background of basic information derived from the literature which is required to intelligently select fluxes for electroslag melting to optimize refining capabilities. It should be emphasized that kinetic and electrochemical effects have been neglected in this chapter. Nevertheless, equilibrium thermochemical calculations provide a basis for estimating possible reactions and optimum conditions in the electroslag process.

ELEMENT PARTITIONING BETWEEN METAL AND FLUX PHASES

Oxygen

Oxygen is important in the electroslag process because it participates in a great number of slag-metal equilibria, particularly when variable valence elements are present, as is usually the case. In a typical electroslag melt in air, the consumable electrode will be oxidized to a certain extent, and the resultant oxides will be dissolved in the molten slag. These oxides eventually reach the slag-ingot interface where reduction occurs and oxygen transfers to the metal. In addition to reduction of the metal oxide, smaller amounts of oxygen can be derived from the initial flux components. This results in gross ingot porosity if the oxygen content is high, or in formation of nonmetallic globular oxide inclusions if the oxy-

gen levels are lower (equation 3). These steps may be expressed in the following reactions:¹



where M is the metal to be melted (usually a transition metal) and R is an alloying element with a high affinity for oxygen such as Si, Al, Ti, or Zr. The degree of oxygen affinity for an element at temperatures of interest can be estimated from the free energies of formation of the appropriate oxides, which are given, for example, by Kubaschewski, Evans, and Alcock (11). The above set of reactions have been confirmed by Buzek and Hlineny (1), who used oxygen isotope methods to trace the oxygen transfer between the phases. The scheme depicted in equations 1-3 is chiefly responsible for loss of easily oxidizable alloying elements during electroslag melting. Experimental results for a number of such elements are given in the literature (1). To minimize oxidative losses during electroslag melting, the oxygen potential in the slag should be kept to a minimum. This can be achieved by (1) minimizing variable valence oxides, (2) minimizing the level of elements which form relatively unstable oxides, (3) eliminating oxidation of the electrode through the use of an inert atmosphere, and/or (4) adding reductants to the electrode and/or flux which form more stable oxides than the oxides which are to be reduced. Silicon is one of the most effective steel deoxidizers in basic fluxes. Consider the reaction



for which the equilibrium constant $[K_{(4)}]$ is

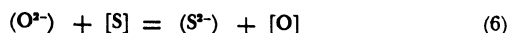
$$K_{(4)} = \frac{a_{SiO_2}}{a_{[Si]} \cdot a_{[O]}^2} \quad (5)$$

¹ In this chapter, $\{ \}$, $()$, and $[]$ refer to gas, slag, and metal phases, respectively.

where a represents the respective activities. In basic fluxes, the CaO combines with the SiO₂, forming calcium silicates in which the activity of silica is considerably less than unity. A correspondingly low value of $a_{[Si]} \times a_{[O]}^2$ would be expected after electroslag remelting under such fluxes. Low oxygen contents are expected if the silicon content in the steel remains within specifications (7). Desirable flux oxide components are those which possess large negative free energies of formation.

Sulfur

One of the most easily transported elements between flux and metal in the electroslag process is sulfur. Therefore, this element is easily removed from molten metal during electroslag melting, provided a suitable flux composition is chosen. In the electroslag process, the transfer of sulfur from the metal to the flux occurs via an exchange of oxygen and sulfur as follows:



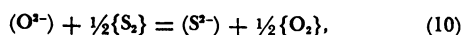
$$\text{for which } K_{(6)} = \frac{\alpha_{[O]} \cdot \alpha_{(S^{2-})}}{\alpha_{[S]} \cdot \alpha_{(O^{2-})}} \quad (7)$$

If we define the distribution coefficient of sulfur between flux and metal as

$$L = \frac{(\text{pct } S^{2-})}{[\text{pct } S]} = \frac{N_{(S^{2-})}}{[\text{pct } S]} \quad (8)$$

$$\text{then } L = K_{(6)} \frac{P_{(O^{2-})}}{[\text{pct } O] \cdot \gamma_{(S^{2-})}} \quad (9)$$

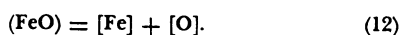
where γ is the activity coefficient, N is the mole fraction, and P is the partial pressure, and we assume Henrian behavior ($a_{[O]} = [\text{pct } O]$). This equation is valid for dilute solutions. Hence, transfer of sulfur from the metal to slag is enhanced by high slag basicity [$>P_{(O^{2-})}$] and low oxygen contents in the metal [pct O]. By combining thermochemical data for reaction 6 and the flux-gas equilibria



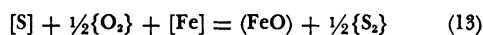
we obtain



and calculation of the theoretical transfer of sulfur from metal to flux is possible. In electroslag melting ferrous alloys, the oxygen content in the metal is related to the activity of FeO in the slag, given by



Combining equations 11 and 12 gives



and the equilibrium constant [$K_{(10)}$] is

$$K_{(10)} = \frac{a_{(\text{FeO})}}{a_{[S]}a_{[\text{Fe}]}} \left(\frac{P_{S_2}}{P_{O_2}} \right)^{\frac{1}{2}} \quad (14)$$

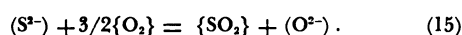
It can therefore be seen that the sulfur content in the metal is proportional to the activity of FeO in the slag² if we assume that $a_s = [\text{pct } S]$,

that $a_{Fe} \approx 1$, that experimental values of $\left(\frac{F_{S_2}}{P_{O_2}} \right)^{\frac{1}{2}}$

as a function of (pct S) have been determined (6, 10), and that each metal droplet reaches equilibrium with the flux prior to freezing during electroslag melting (3). Hence it is desirable to maintain low iron oxide activities (that is, low oxygen potentials) in the slag, not only for oxygen removal, but also for minimizing sulfur in the ingot.

A combination of experimental work and theoretical calculations has shown increasing desulfurization capabilities with respect to the sulfur distribution coefficient (equations 8 and 9) in the series of flux components MgO, CaO, and BaO (8). The superior desulfurization capabilities of highly basic fluxes containing BaO have also been confirmed by Powley and Floridis (14).

Desulfurization can also be enhanced through the transfer from the slag to the gas phase by the reaction



In this case,

$$L = K_{(15)} \frac{P_{S_2}\{O_2\}}{N_{(O^{2-})}\gamma_{(S^{2-})}} \quad (16)$$

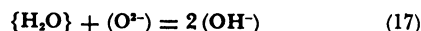
where L is the distribution coefficient of sulfur between gas and flux [that is, $\frac{\{\text{pct } SO_2\}}{(\text{pct } S)}$] and the other terms correspond to those previously defined in this chapter. Based on the foregoing equilibrium estimations, sulfur transfer from the slag to the gas phase is promoted by a high oxygen partial pressure in the gas phase and a low slag basicity [that is, $N_{(O^{2-})}$, which is proportional to the lime content in fluxes with low Al₂O₃ and SiO₂].

Hydrogen

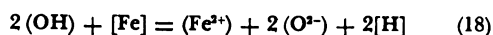
In contrast to vacuum-arc melting, the electroslag process usually does not remove hydrogen

² The slag components are CaO and CaF₂.

from the metal. To understand hydrogen transport in the electroslag process, a determination of the species in the gas, flux, and metal phases is necessary. Flux composition is important in this respect. If CaO is present (for example, in highly basic fluxes), an increase in hydrogen in the metal is likely. Slag preparation and starting techniques may also have some influence. Pocklington (13) has outlined a series of gas-flux and slag-metal reactions whereby hydrogen could be increased in the metal. Water vapor in the atmosphere can react with the flux as follows



if it is assumed that hydrogen is present as the OH^- ion in the flux, although some controversy continues to exist regarding this (12). In the case of CaO in the flux, this would react with water vapor to form $Ca(OH)_2$. The hydrogen in the slag is then transported to the liquid metal where further reactions such as



occur. It is believed (13) that in the case of hydrogen in ferrous alloy electroslag melting, the slag-metal interface is the important reaction site. Therefore, since

$$K_{(18)} = \frac{a_{[H]}^2 \cdot a_{(O^{2-})}^2 \cdot a_{(Fe^{2+})}}{a_{[Fe]} \cdot a_{(OH^-)}^2}$$

then

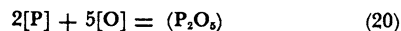
$$[H] = \left[\frac{K_{(18)}}{a_{(Fe^{2+})}} \right]^{1/2} \frac{a_{(OH^-)}}{a_{(O^{2-})}}, \text{ if } a_{[Fe]} = 1. \quad (19)$$

Hence, hydrogen in the metal is minimized with a high oxygen potential in the slag (that is $> FeO$).

In addition, it has been observed (13) that the use of dc reverse polarity tends to favor reaction 17. However, (OH^-) transport to the electrode shifts the equilibrium of reaction 17 to the left. In dc straight polarity melts, (OH^-) would be removed from the electrode. In the case of the slag-metal interface reactions, straight polarity dc would discourage increases in hydrogen in the metal, whereas dc reverse polarity melting results in hydrogen pickup. Electrolytic reactions at the slag-metal interface are probably responsible for the observed differences in ingot hydrogen as a function of melting mode (dc+, ac, dc-, in order of decreasing ingot hydrogen pickup). Low ingot hydrogen would be inversely related to the activity of FeO in the slag.

Phosphorus

Phosphorus removal from metal in the electroslag process can be achieved by oxidation:



where

$$K_{(20)} = \frac{a_{(P_2O_5)}}{a_{[P]}^2 \cdot a_{[O]}^5} = \frac{\gamma_{(P_2O_5)} \cdot N_{(P_2O_5)}}{a_{[P]}^2 \cdot a_{[O]}^5} \quad (21)$$

For maximum dephosphorization, a high value of $a_{[O]}$ and a low value of $\gamma_{(P_2O_5)}$ are required. These can be achieved by using fluxes high in CaO, because the strong interaction of CaO and P_2O_5 to form very stable phosphates reduces $\gamma_{(P_2O_5)}$. High oxygen activities can be attained with a high FeO content in the slag. Davies, Hawkins, and Smith (4) have confirmed this conclusion on the basis of thermochemical calculations using the sparse data presently available. It follows that for effective dephosphorization, minimal SiO_2 contents in the slag are also required.

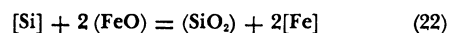
Nitrogen and Carbon

Very little information is available regarding the thermochemistry of nitrogen in electroslag melting. In most cases, nitrogen contents do not appear to vary significantly between electrode and ingot metal.

Essentially, much of the carbon present in the slag as a result of prefluxion or additives will be transferred to the metal during electroslag melting. Transport is presumably by means of carbide ions oxidized to carbon.

Silicon

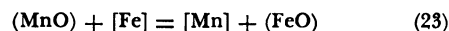
When fluxes with high levels of CaO are used, there is a tendency for much of the silicon present in the electrode metal to be oxidized. In this case, formation of calcium silicates in the slag reduces the silica activity, and the reaction



proceeds to the right.

Elements of Variable Valence

Manganese additions to ferrous ingot metal are relatively easily accomplished during electroslag melting because of the high activity coefficient of MnO (γ_{MnO}) in commonly used slags. The reaction of interest is

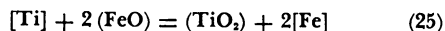


where

$$K_{(23)} = \frac{a_{[Mn]} \cdot a_{(FeO)}}{a_{[Fe]} \cdot a_{(MnO)}} = \frac{a_{[Mn]} \cdot \gamma_{(FeO)} \cdot N_{(FeO)}}{a_{[Fe]} \cdot \gamma_{(MnO)} \cdot N_{(MnO)}} \quad (24)$$

Experimental data (3) show that considerable amounts of manganese can be alloyed with iron while the concentration of MnO remains relatively small in the slag.

In the case of titanium, it is usually desired to retain this element in the metal. This requires a low activity of FeO in the slag, according to the following reaction:



where

$$K_{(25)} = \frac{a(\text{TiO}_2) \cdot a_{[\text{Fe}]}^2}{a_{(\text{FeO})}^2 \cdot a_{[\text{Ti}]}} \quad (26)$$

EQUILIBRIUM THERMODYNAMICS OF FLUXES

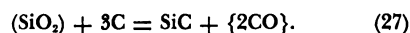
Element transfer between flux and metal in the electroslag process is dependent to a great extent on the thermodynamics of the flux phase. Available high-temperature activity data for components of common fluxes (for example, CaF_2 , CaO , MgO , Al_2O_3) are sparse, and when available, often conflict with each other.

Edmunds and Taylor (5) have determined lime activities in the important flux system CaF_2 - CaO - Al_2O_3 at 1,500° C based on vapor pressure determinations of CO in equilibrium with CaO in the flux, C, and CaC_2 . The lime activity increases much more rapidly with increasing lime content as the total Al_2O_3 concentration increases. A negative deviation from Raoult's law is indicated for CaF_2 levels less than approximately 50 weight-percent and Al_2O_3 concentrations greater than 20 weight-percent. These authors also summarize lime activities at 1,500° C for the binary joins CaO - Al_2O_3 and CaO - CaF_2 . In the join CaO - Al_2O_3 negative deviations are shown for lime concentrations less than approximately 68 mole-percent CaO, whereas positive deviations are indicated for greater CaO levels. For the CaO - CaF_2 join, positive deviations for the lime activity are shown for 1,500° C. Hawkins, Meherali, and Davies (6) show CaF_2 activities with a slight negative deviation from ideality up to 30 mole-percent CaO at 1,500° C.

Although compositions involving large amounts of SiO_2 are not normally used as electroslag fluxes owing to adverse physicochemical properties, this compound can become a significant factor when ferrosilicon is used to deoxidize the metal. Silica also has a definite effect on the oxygen content and nonmetallic inclusion level in an ingot.

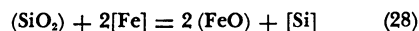
Sommerville and Kay (15) have determined silica activities in the system CaF_2 - CaO - SiO_2 at

1,450° C by measuring the equilibrium partial pressure of carbon monoxide for the reaction



These authors obtained low values for the activity coefficient of silica, ranging from 0.03 to 0.22 in the composition range 6 to 27 mole-percent SiO_2 . Between 40 and 80 mole-percent CaF_2 , the isoactivity curves parallel lines of constant CaO - SiO_2 ratio. The silica activity is extremely sensitive to compositional changes near the CaF_2 apex and could be a major factor in controlling the oxygen content in electroslag-melted steel (7). Activities of CaO were calculated using a ternary integration of the Gibbs-Duhem equation. These results also show large negative deviations from ideality.

As the slag basicity decreases, the activity of SiO_2 in the slag generally increases. For example, in a slag of low basicity, the slag-metal reaction



can occur at temperatures of interest (11). Thus, the iron oxide content of the slag increases and silicon reports to the ingot metal. On the other hand, slags having a high basicity usually contain considerable CaO, and a reaction analogous to reaction 28 would not occur at high temperatures from a thermochemical standpoint (11).

In the system CaF_2 - CaO -" FeO ", Kay, Mitchell, and Ram (9) have determined the activity of " FeO " at 1,410°-1,500° C by studying the equilibrium



Positive deviations from ideality are indicated up to 10 mole-percent FeO. These decrease as the CaO content increases. This means that relatively small quantities of FeO in the slag will exert a great influence on the oxygen potential.

Determinations of the activity of MnO in the system CaF_2 - CaO -MnO at 1,500° C by Davies and Smith (2) also indicate large positive deviations from ideality. These also decrease with increasing CaO contents at a more rapid rate than is the case for FeO. This is attributed to solid solubility between CaO and MnO, reflecting the greater affinity of MnO for CaO than for CaF_2 .

CONCLUSION

Thermochemical data to optimize flux compositions for electroslag melting are sparse. Until more data and evaluations of applicable complex systems become available, empirical selections will predominate.

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* Titles enclosed in parentheses are translations from the language in which the item was published.

CHAPTER 4.—HEAT TRANSFER TO WATER-COOLED CRUCIBLES DURING ELECTROSLAG MELTING

By Staff, Albany Metallurgy Research Center

This chapter describes a limited number of experiments conducted by the Bureau of Mines in which the rates of heat transfer from the crucible to the cooling water during electros slag melting were measured. These data are of interest because they provide a better understanding of the electros slag melting process, particularly as related to ingot solidification, pool depth, and melting efficiency. The experimental technique used for measuring heat transfer from the crucible during electros slag melting was based on similar measurements of heat transfer during consumable-electrode vacuum-arc melting. Results of the arc-melting work were published previously (2).

Vacuum-arc melting and electros slag melting are similar in that both utilize a consumable electrode and a water-cooled copper crucible. Furnaces designed for vacuum-arc melting have been used for electros slag melting with only minor modifications, as described in chapter 7. In other respects, the two techniques differ greatly. In electros slag melting, heat is generated by resistive heating of the molten slag, and heat losses from the molten slag to the crucible result in less efficient melting of the electrode. A major advantage of electros slag melting is the flat, shallow pool of molten metal maintained in the crucible during melting. Because of these differences, one would expect the distribution of heat transferred from the crucible to the cooling water during electros slag melting to be considerably different from that observed during vacuum-arc melting.

EXPERIMENTAL METHOD

The initial attempts to measure heat transfer during electros slag melting were made in equipment used for the study of heat transfer during consumable-electrode vacuum-arc melting. The crucible used for these initial attempts is shown in figure 16. This crucible was 10.2 cm (4 inches) in diameter. The lower section of the sidewall

was 15.2 cm (6 inches) long, and the upper section was 20.3 cm (8 inches) long. With this crucible, data on coolant flow rate and coolant inlet and outlet temperatures to each of the three sections provided a measure of the rate of heat transfer to each section. Ingot length, as a function of time, was calculated from measurements of electrode movement during melting.

Figure 17 shows the rates of heat transfer to each of the three sections of this crucible during electros slag melting of titanium. In this run, a 5.1- by 5.1-cm (2- by 2-inch) titanium sponge electrode 76.2 cm (30 inches) long was melted at 4,800 amperes and 27 to 28 volts (direct current, electrode negative) in approximately $\frac{1}{3}$ atm of helium. For starting, a 1.27-cm ($\frac{1}{2}$ -inch) thick titanium starting pad 7.6 cm (3 inches) in diameter was placed in the bottom of the crucible with ~ 200 grams (0.44 pound) of loose titanium sponge. The electrode was shorted to this base, and 1.135 kg ($2\frac{1}{2}$ pounds) of granular calcium fluoride was added. Melting was initiated at 1,400 amperes and approximately 30 volts, and power input was then increased as rapidly as possible and held constant throughout the remainder of the run. Full power was achieved after 1 minute and 40 seconds; melting was completed in 9 minutes and 55 seconds. The final ingot was 24.4 cm ($9\frac{5}{8}$ inches) long, and the slag cover was 5.4 cm ($2\frac{1}{8}$ inches) thick at the end of the run.

Figure 17 also includes the curve representing total heat transfer to all sections of the crucible. A heat balance based on the area under this curve indicated that 96 percent of the total energy supplied during melting was removed by the crucible cooling water. The remaining 4 percent represents losses to the other furnace sections such as the electrode holder and main furnace body. Included in the total heat transferred to the upper crucible section was 82 percent removed during melting, 14 percent removed after melting was completed, and only 3

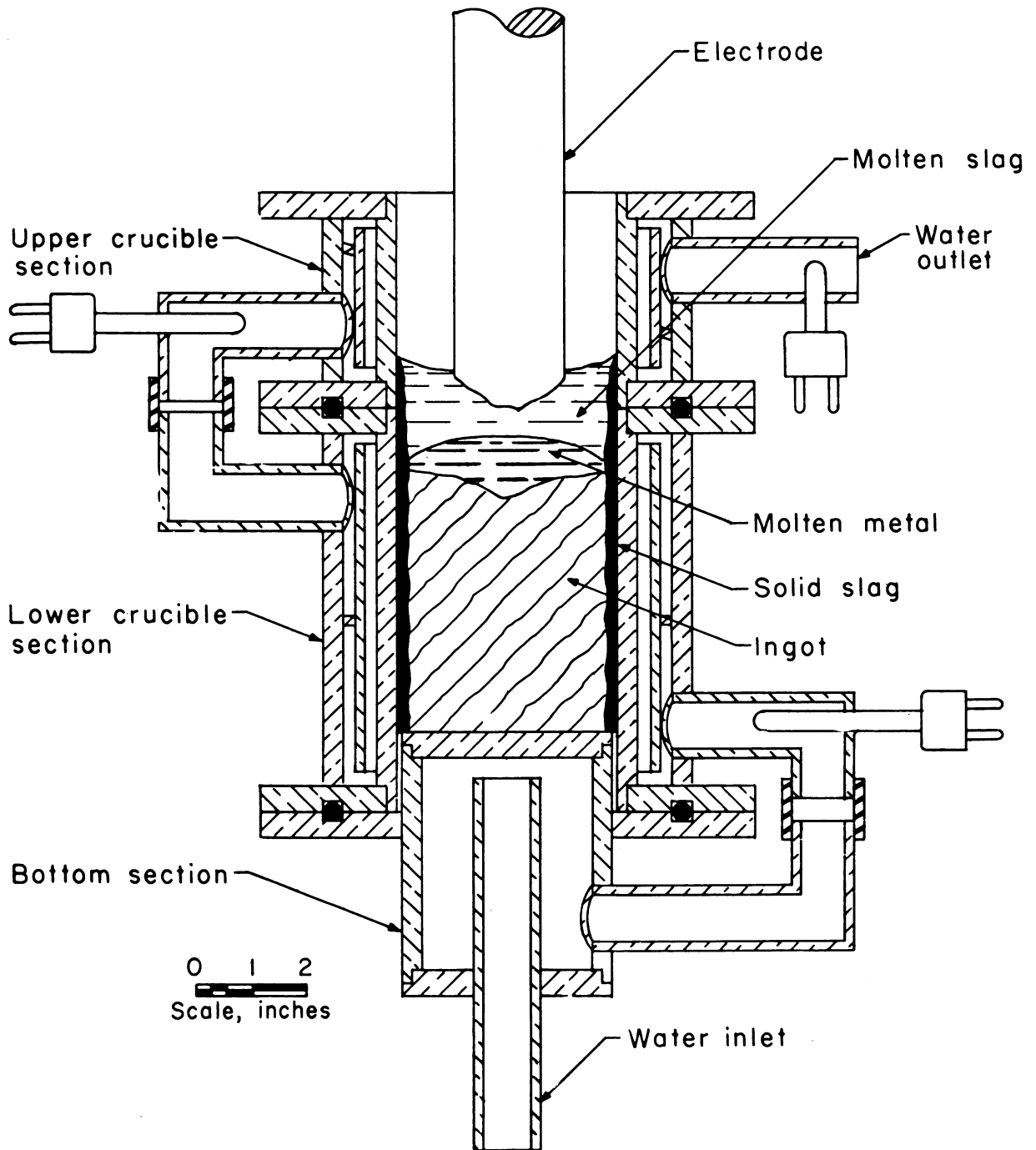


Figure 16.—Three-piece crucible for measuring heat transfer to cooling water during electroslag melting.

percent removed at the crucible bottom. The 14 percent removed after melting was completed represents heat stored in the ingot and slag. Also included in the 96 percent was most of the heat

radiated from the upper surface of the slag and from the hot electrode.

Attempts to utilize the data shown in figure 17 for calculating a profile of radial heat flux

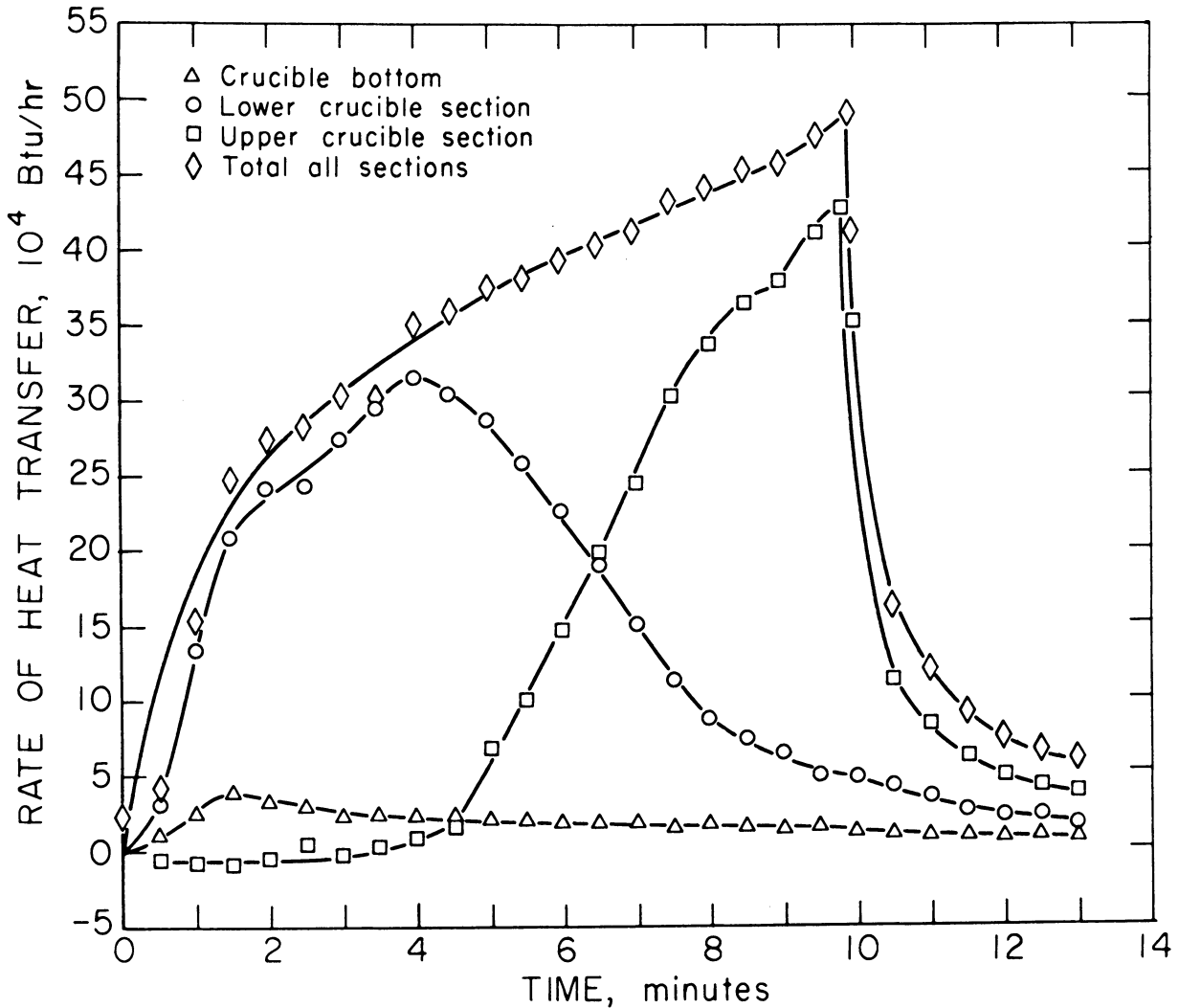


Figure 17.—Rate of heat transfer to crucible during electroslag melting of titanium.

along the length of the ingot during electroslag melting were unsatisfactory. This technique had been used successfully for calculating heat flux profiles during consumable-electrode arc melting and has been described in detail (2). The technique was based on the assumption that the radial heat flux profile did not change appreciably with changes in ingot length once the ingot was at least 10 cm (one diameter) long. Any change in the rate of heat transfer to the upper crucible section resulted from movement of the heat flux profile relative to the upper crucible section as ingot length increased. With each incremental increase in ingot length, the upper crucible section was exposed to an addi-

tional increment of the heat flux profile. For example, during the time the ingot length changed from 15.2 to 16.5 cm (6 to 6½ inches), the observed increase in rate of heat transfer to the upper crucible section represented the heat transferred from the upper 1.27 cm (½ inch) of ingot. The average heat flux in Btu per hour-square foot¹ for this 1.3 cm of ingot was determined by dividing the change in the rate of heat transfer by the incremental change in sidewall area of the ingot. A similar calculation of heat flux could be made for any increment of ingot length. Thus, the slope of the curve of rate of heat

¹ 1 Btu/hr-ft² = 0.271 cal/hr-cm² or 2.713 kcal/hr-m².

transfer to the upper crucible section plotted as a function of ingot length was proportional to the heat flux.

When this technique was applied to the data for electroslag melting shown in figure 17, results were unsatisfactory because of apparent scatter of data during the latter part of each run. Attempts to determine the slope of this curve were complicated by what appeared to be excessive experimental error. Because of these difficulties, an alternate technique for measuring heat flux had to be devised.

Figure 18 shows the crucible modification designed to measure heat flux during electroslag melting by this alternate technique. This modification consisted of a separate, 0.64-cm ($\frac{1}{4}$ -inch) long section placed between the upper and lower crucible sections. This short section was separately cooled, and data on coolant flow rates and inlet and outlet temperatures provided a direct measure of the average heat flux to the 0.64-cm ($\frac{1}{4}$ -inch) length of crucible during melting. Data obtained with this crucible during melting of a mild steel electrode are shown in figure 19. In this run, an electrode made by welding nine, 1.91-cm ($\frac{3}{4}$ -inch) steel reinforcing bars into a

bundle was electroslag-melted using calcium fluoride slag. This electrode was melted with direct current, electrode negative, at 3,400 amperes and 30 volts. The sharp fluctuations in heat flux shown in figure 19 were the cause of the difficulties experienced in the interpretation of the data obtained with the crucible shown in figure 16.

DISCUSSION

Figure 19 shows three peaks in the heat flux pattern: one at the upper surface of the slag, one midway between the upper and lower surface of the slag, and one at the metal pool-slag interface. The peak at the upper slag surface was attributed to molten slag contacting the crucible wall as the upper surface moved upward in the crucible. In these runs it was difficult to determine the exact location of the upper slag surface during melting because of displacement of the slag by immersion of the electrode. Location of the upper surface of the slag in figure 19 was based on estimates of the displacement of the slag by immersion of the electrode and is believed accurate within ± 0.64 cm ($\frac{1}{4}$ inch). Immediately below the upper peak was a region in

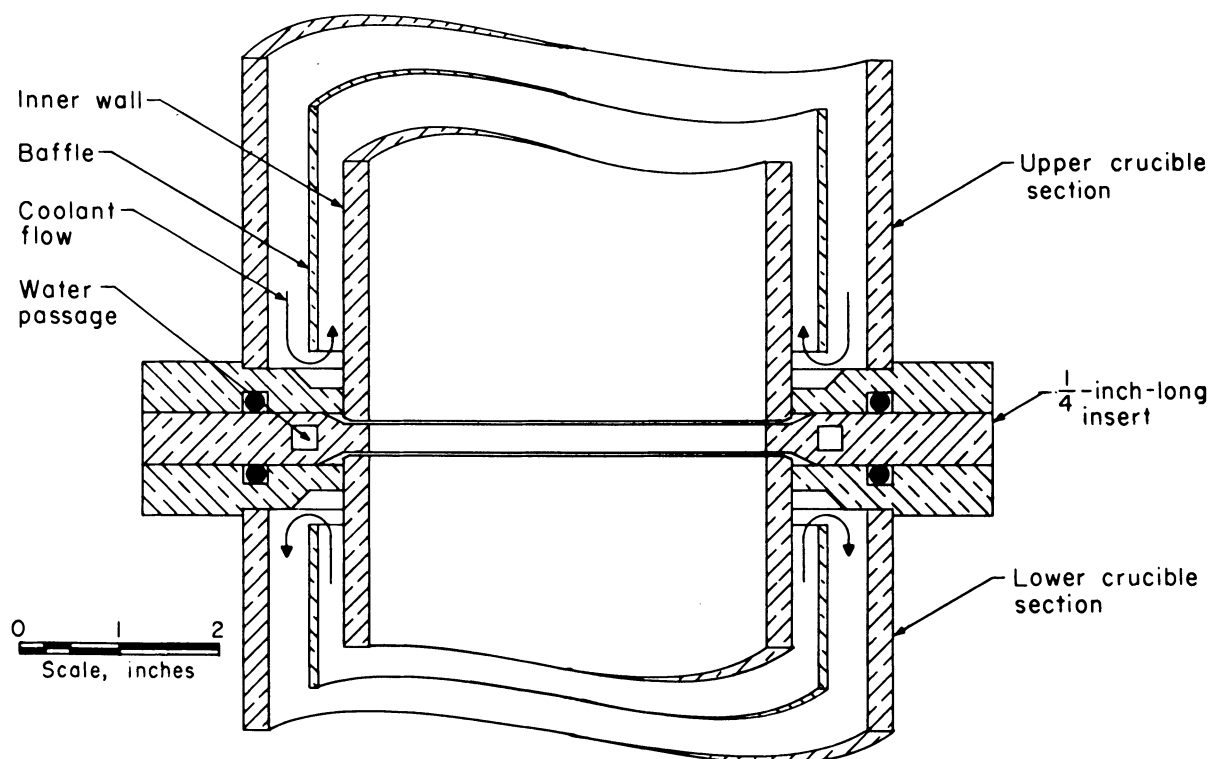


Figure 18.—Crucible modification for direct measurement of heat flux during electroslag melting.

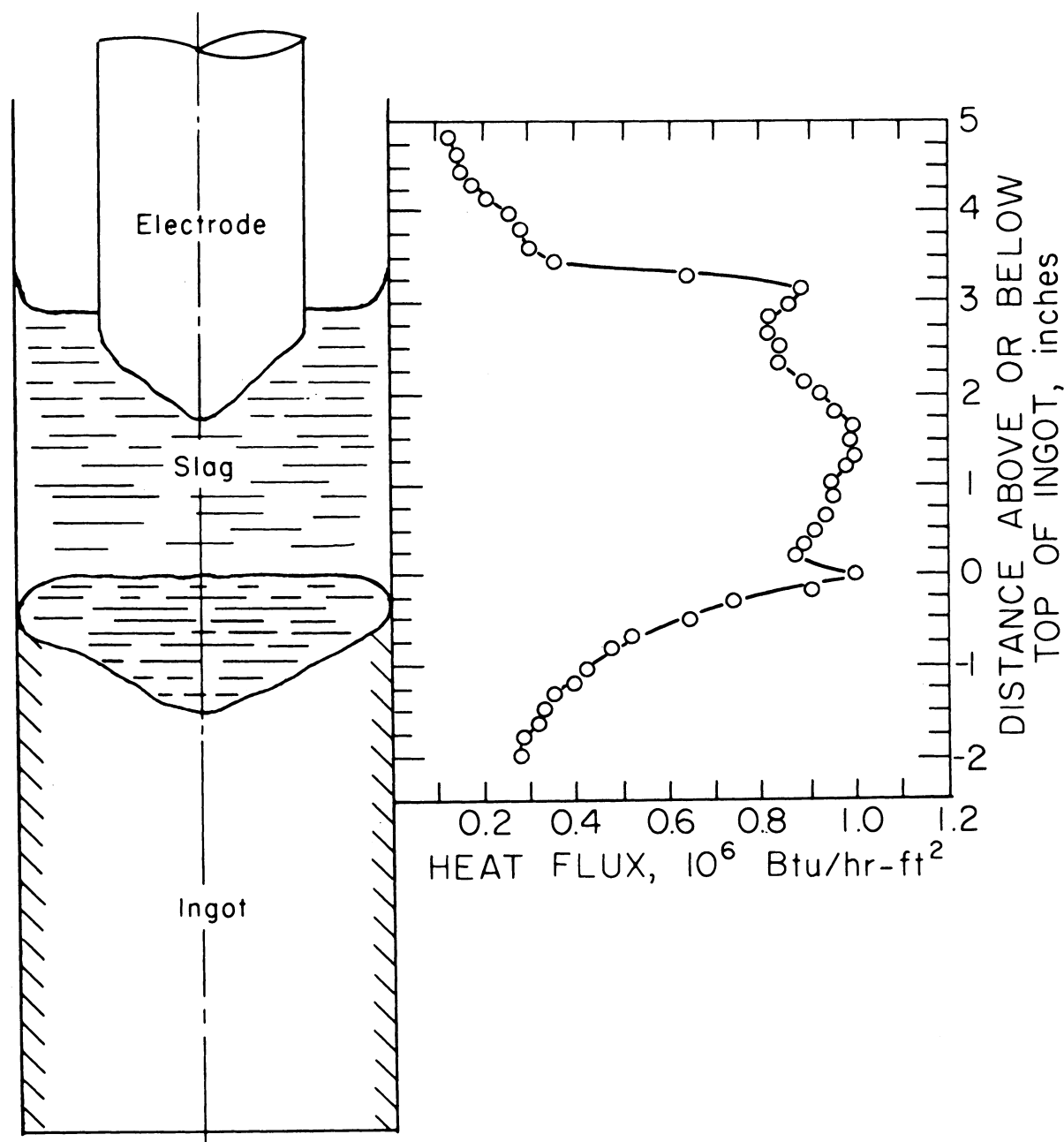


Figure 19.—Distribution of radial heat flux during electrosag melting of 4-inch-diameter mild steel ingot. Coolant flow rate = 2.4 gal/min.

which the heat flux decreased slightly. This was attributed to shrinkage of the solidified slag skin that formed.

Higher rates of heat transfer noted near the middle of the slag pool resulted from heat generation within the slag by passage of current from the lower end of the electrode to the up-

per surface of the ingot. The effect of this heating decreased in the lower part of the slag. Campbell (1) reported a cool boundary layer immediately above the metal pool-slag interface during consumable-electrode electrosag melting in a transparent crucible.

The sharp peak at the upper surface of the

ingot shows a zone of high rates of heat transfer associated with the molten metal pool. Mitchell and Joshi (4) describe the molten metal pool as having a cylindrical portion; that is, a finite length of the ingot sidewall is molten at the upper surface of the ingot. High rates of heat transfer would be expected where molten metal from the pool was separated from the mold wall by only a thin skin of solidified slag. It would be of considerable interest to conduct sufficient additional experiments to correlate ingot sidewall quality and a characteristic heat flux profile. Variations in slag composition, electrode diameter, and power input would also be of interest in such a study.

Of the total heat transferred to the crucible during the run shown in figure 19, 14 percent occurred above the top surface of the slag as radiation from the hot electrode and the upper slag surface. Heat transfer from the slag to the crucible accounted for 59 percent of the total, and 27 percent of the total derived from the ingot. Holzgruber and Plöckinger (3), in a similar study during electroslog melting of iron, reported 20 percent removed by radiation loss and 80 percent transferred to the crucibles.

Additional runs were made in this crucible but not in sufficient number to warrant any conclusions regarding the effects of such variables as electrode diameter, melting current, voltage, slag depth, and slag composition on the shape of the heat flux profile and the interrelationship between the heat flux profile and ingot quality. In all the runs, the heat flux profile was characterized by three peaks similar to those shown in figure 19. While the values of the peak heat flux varied for different runs, the same zones of high heat flux were noted in all. It was evident from the limited number of runs conducted that minor variations in any of the many variables associated with electroslog melting altered the shape of the heat flux profile.

CONCLUSIONS

The results reported in this chapter were based on a very limited number of tests and should be considered no more than tentative

indications of heat flux patterns during electroslog melting. Even though the present study was limited, several conclusions can be made.

Heat transfer to the crucible bottom during electroslog melting represented a small portion (3 percent) of the total heat transfer to the crucible. It should be noted, however, that a large portion of the total heat transfer occurred between the slag cover and the crucible so that the heat transfer to the crucible bottom did represent a proportionately larger percentage of the heat transfer from the ingot itself.

The heat flux profile during electroslog melting was characterized by three peaks. One occurred at the upper surface of the slag and represented heat transfer to the crucible from molten slag contacting the wall as the slag pool moved upward in the crucible. Directly below this region of high heat flux was a region of slightly lower values of heat flux that resulted from solidification of a slag skin and shrinkage of this skin away from the wall. Heat flux values increased to a second peak somewhere along the wall of the slag cover. This increase in heat flux resulted from heating of the slag by electrical current flow from the electrode to the ingot.

Values of heat flux decreased near the bottom of the slag pool, and a third peak in the heat flux profile occurred at the upper surface of the ingot. The decrease in heat flux along the lower part of the cover may have been an indication of the pattern of heat generation within the molten slag pool and/or the effect of increasing thickness of the layer of solid slag that formed against the copper wall. The ingot top, where liquid metal was in contact with the inner surface of the solid slag layer, was also a zone of high heat flux. Heat flux below the ingot top should drop off rapidly as the ingot solidified and shrank away from the wall.

A further study of heat transfer to the crucible during electroslog melting should be made to determine the effects of the many variables associated with this melting technique. Such a study should provide a better understanding of the relationship between these variables and the quality of the resulting ingots.

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CHAPTER 5.—FLUORIDE FLUX SYSTEMS FOR ELECTROSLAG MELTING¹

By R. H. Nafziger, R. L. Lincoln,² and N. Riazance³

Electroslag melting of reactive metals places great restrictions on possible suitable flux compositions. Desirable flux characteristics for the electroslag process include the requirements that (1) the liquidus temperature of the flux should be slightly below that of the metal to be melted, (2) the density of the flux must be less than that of the metal at its melting point, and (3) the electrical conductivity of the flux should be as low as possible for economical operation (less than that of the metal but high enough to permit a stable melting operation and to permit a thin flux skin to form between the ingot metal and the mold to prevent possible arcing or mold-wall puncture). Halides are the most suitable anionic materials since, for example, molten titanium getters oxygen from the more common oxides used in steelmaking fluxes. Borides, carbides, and nitrides melt at temperatures too high for practical use (2,200° to 3,900° C) or decompose at <1,000° C. Alkali and transition metal halides as well as most chlorides, bromides, and iodides invariably possess unsuitably high vapor pressures and are otherwise unstable at temperatures and pressures of interest. Appropriate flux compositions for melting reactive metals are thus limited to alkaline-earth and lanthanon (rare earth + yttrium) fluorides.

Thermochemical calculations (table 5) indicate that such compounds would not react with molten titanium at 1,727° C (2,000 K), a temperature believed to be approximately that achieved during the electroslag melting of titanium.

Group IIA fluorides may be subdivided, primarily on the basis of the radii of the cations, into two classes which, in turn, largely determine

the coordination numbers of the ions and the crystal structures. The classes include those compounds with cationic radii⁴ (in angstroms) which are (1) <1.0, for example, BeF₂—0.35 (0.34) and MgF₂—0.80 (0.78); and (2) >1.0, for example, CaF₂—1.20 (1.06), SrF₂—1.33 (1.27), BaF₂—1.50 (1.43), and RaF₂—1.56 (1.52).

ALKALINE-EARTH FLUORIDE SYSTEMS

Few high-temperature investigations have been conducted to characterize liquidus temperatures in alkaline-earth fluoride systems. Berezhnaya and Bukhalova (3), Rolin and Clausier (26), and Lukashenko and Reutova (20) investigated the system BaF₂—CaF₂—MgF₂. Zhigarnovskii and Ippolitov (37) reported on the system CaF₂—BaF₂; Weller, Axe, and Pettit (33) inferred phase relations in the CaF₂—SrF₂ system. Bukhalova, Mateiko, and Berezhnaya (4) and Mateiko and Bukhalova (21) assumed a continuous series of solid solutions for the BaF₂—SrF₂ system, but these authors made no attempt to verify the relations. The aforementioned literature indicates that binary combinations of class 1 and class 2 alkaline-earth fluorides yield systems with one or more eutectics and no discernible solid solutions. On the other hand, indications are that binary systems of class 2 fluorides generally possess extensive solid solutions. The BaF₂—SrF₂ system was selected for experimental study to (1) verify the above assumption regarding class 2 fluorides, and (2) determine whether this system would act as a suitable flux for electroslag melting reactive metals.

Powdered mixtures were prepared by heating reagent-grade fluorides in the presence of excess NH₄F•HF to ≈900° C for several hours in a graphite resistor furnace which had been evacu-

¹ Adapted from J. Am. Ceram. Soc., v. 54, 1971, p. 467; J. Am. Ceram. Soc., v. 55, 1972, pp. 130–134; J. Inorg. Nucl. Chem., v. 35, 1973, pp. 421–426.

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⁴ The first values given are the radii of Whittaker and Muntus (34) for cationic coordination numbers of 4 and 6 for group 1 and of 8 for group 2. These values have been modified from those given by Shannon and Prewitt (28). Values in parentheses are Goldschmidt radii (11) which do not account for coordination numbers.

Table 5.—Standard free energies of reaction at 1,727° C (2,000° K)

Slag () and metal []	Calculated ΔG° , kcal		
	$n = 2$	$n = 3$	$n = 4$
$n/2$ (MgF ₂) + [Ti] = (TiF _n) + $n/2$ [Mg]	+11	+16	+43
$n/2$ (CaF ₂) + [Ti] = (TiF _n) + $n/2$ [Ca]	+46	+68	+113
$n/2$ (SrF ₂) + [Ti] = (TiF _n) + $n/2$ [Sr]	+42	+62	+105
$n/2$ (BaF ₂) + [Ti] = (TiF _n) + $n/2$ [Ba]	+54	+80	+129
$n/3$ (YF ₃) + [Ti] = (TiF _n) + $n/3$ [Y]	+17	+24	+55
$n/3$ (LaF ₃) + [Ti] = (TiF _n) + $n/3$ [La]	+36	+35	+69
$n/2$ (CaCl ₂) + [Ti] = (TiF _n) + $n/2$ [Ca]	+56	+96	+128

Source: Data obtained from reference 31 for MgF₂ and TiF_n, from reference 10 for CaCl₂, and from reference 35 for all others.

ated to 10^{-2} torr pressure. The samples were contained in a liner of TZM, a molybdenum-based commercial alloy (0.02 wt-pct C, 0.5 wt-pct Ti, 0.08 wt-pct Zr, balance Mo). The heated powders were weighed in the correct proportions, ground, mixed, and stored in desiccators. Treated mixtures used as starting materials contained typical total impurities of 0.07 to 0.91 percent with Al, Ca, Mo, and Na as the major components. Since high-temperature ($>1,000^\circ$ C) solid phases in the fluoride systems under investigation cannot be conveniently quenched for study, thermal analysis, including DTA, is particularly well suited for determinations in these systems. Standard DTA techniques were therefore used to determine the liquids and solidus temperatures and the possible solid-phase transitions of each mixture. Nuclear-grade graphite crucibles containing the mixtures were placed in a furnace with a tantalum resistance heating element surrounded by a water-cooled copper crucible. The reference materials was α -Al₂O₃, and temperature was measured with W3Re-W25Re thermocouples which had been checked against the melting points of copper and nickel, based on the International Practical Temperature Scale of 1968. The furnace was pumped to $\approx 3 \times 10^{-5}$ torr pressure and backfilled to $1/3$ atm He, approximating atmospheric conditions of furnaces used for electrosag melting of reactive metals in this laboratory. Such a treatment of fluoride systems does not cause significant changes in mixture composition by selective volatilization. Constant heating and cooling rates of 29° and 22° C min⁻¹, respectively, were obtained by a motor-driven variable transformer. Phases were identified by optical microscopy and X-ray diffraction after each experiment.

Results of these determinations are presented in figure 20. Complete solid solubility is evident, with a shallow minimum of the liquidus curve

at $\approx 27 \pm 2$ weight-percent SrF₂ and $1,305^\circ$ C ($\approx 40^\circ$ and 160° C below the melting points of BaF₂ and SrF₂, respectively). The liquidus temperatures increase from the indifferent point to pure SrF₂. The melting point of SrF₂ is $\approx 200^\circ$ C below that of titanium and 50° C above that of CaF₂, which is the most commonly used flux for melting reactive metals. (See chapters 7 and 10.) No evidence of a solid miscibility gap was detected above 850° C, as would be expected at lower temperatures on the basis of ionic field strengths, cationic radii, and thermodynamic considerations. The melting point temperatures determined for BaF₂ and SrF₂ are within the ranges reported in the literature (18, 25–26).

SYSTEMS CONTAINING LaF₃

Compounds with potential for application in the electrosag process in both classes 1 and 2 were then selected for study with LaF₃. The melting point of LaF₃ is $\approx 90^\circ$ C higher than that of CaF₂. In addition, LaF₃ is more stable than CaF₂ at the high temperatures involved in electrosag melting.

The systems CaF₂–LaF₃, SrF₂–LaF₃, BaF₂–LaF₃, and MgF₂–LaF₃ were studied because it was thought that they were most likely to form high-melting-point compounds, intermediate phases, and/or dystectics.⁵ Such characteristics should decrease the temperature interval between the liquidus temperature of the flux and the melting point of the reactive metals such as titanium and zirconium and thus improve the surfaces of the melted metal. Relative high-temperature stabilities, the existence of a dystectic in an analogous YF₃ system (29), and high-

⁵ The term dystectic, as used in this work, denotes a point of maximum temperature on the liquidus curve where the compositions of two equilibrium phases become identical and the system loses one degree of freedom. This definition follows previous usage (36).

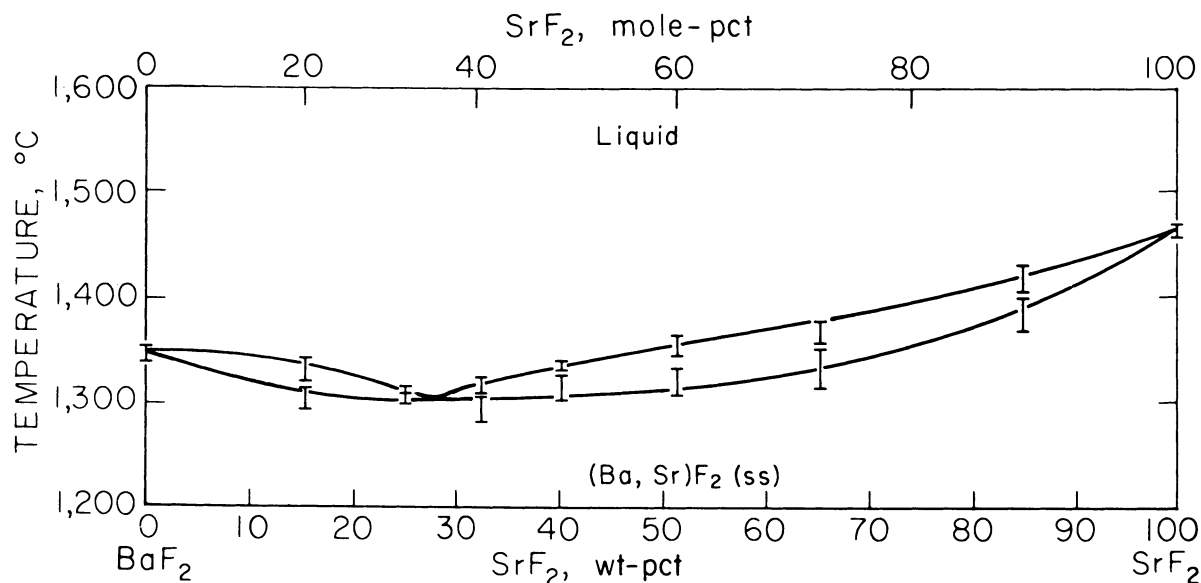


Figure 20.—High-temperature phase relations at $\frac{1}{3}$ atm He pressure in the system BaF_2 – SrF_2 . Length of each vertical line indicates 1 standard deviation for replicate liquidus and solidus temperature measurements for each composition studied.

temperature compatibility with reactive metals were also considered in selecting these systems.

Literature data for these systems at high temperatures are also scanty. Ippolitov and coworkers (13–14) presented results on the subsolidus phases in systems containing LaF_3 but gave no data on liquidus temperatures. Zagorskaya, Ivanova, and Maksakov (36) reported four eutectics and four dystectics in the CaF_2 – LaF_3 system but did not specify the atmosphere used; their diagram may have resulted from excessive hydrolysis or nonequilibrium conditions. Ippolitov, Gogadze, and Zhigarnovskii (15), however, obtained a diagram for this system in argon similar to that derived in the present work, and Zhigarnovskii and Ippolitov (38) published a phase diagram for the system BaF_2 – LaF_3 in 1.5 to 2 atm argon. Hahn, Seemann, and Kohn (12) studied lattice parameters and room-temperature densities in fluorite solid-solution phases in several systems containing LaF_3 at 1,200° and 1,400° C, but reported neither solidus nor liquidus temperatures.

Experimental Method

The experimental method was similar to that described previously in this chapter except that most of the determinations were conducted in a water-cooled graphite resistor furnace supplied with dc power. The emf values from a

columbium-sheathed W3Re–W25Re thermocouple inserted into the sample were recorded as a function of time on calibrated adjustable-zero, adjustable-range, millivolt, potentiometric recorders to provide the necessary heating and cooling curves. The thermocouple was calibrated⁶ frequently against the freezing points of oxygen-free copper and Grade I nickel, neither of which contained spectrographic impurities >0.3 ppm. No reactions between the thermocouple, sheath, sample, and crucible were observed. Before each run, the furnace was pumped to $\approx 10^{-2}$ torr and then backfilled with helium to $\frac{1}{3}$ atm total pressure. Samples were heated to $\approx 50^\circ$ to 100° C above the liquidus temperatures and cooled. Heating and cooling rates were typically 30° and 25° C min^{-1} , respectively.

Initial changes in the slopes of the cooling curves identified the liquidus temperatures; solidus temperatures were determined from the heating curves when the solidus curves were relatively steep. The samples were observed visually with an optical pyrometer during heating and cooling to verify the solidus and liquidus determinations. Variance in the temperature measurements was estimated from several replicate runs on each mixture. After thermal analysis runs,

⁶ On the basis of the International Practical Temperature Scale of 1968 (27).

samples were usually analyzed spectrographically for impurities, assayed for carbon and nitrogen, and observed by microscopy under reflected light. Phases were identified by powder X-ray diffraction methods, occasionally supplemented by electron microprobe examination. X-ray lattice parameters were determined at room temperature on samples which had been held at constant temperature for 20 to 75 minutes and quenched by shutting off the furnace power. Such times are consistent with those used in electroslag melting practice.

The techniques described resulted in samples whose bulk compositions did not change significantly during thermal analysis, as is illustrated in table 6 for mixtures in the system $\text{CaF}_2\text{--LaF}_3$. The average total weight loss of the $\text{CaF}_2\text{--LaF}_3$ samples during the runs was 1.8 weight-percent of the amount present. Comparable differences were observed in the other systems. Supplemental differential thermal analysis on selected compositions in each of the systems containing LaF_3 was conducted under conditions described for the alkaline-earth fluoride work in this chapter.

Results

Liquidus and solidus boundaries determined from the heating and cooling curves for the systems $\text{CaF}_2\text{--LaF}_3$, $\text{SrF}_2\text{--LaF}_3$, $\text{BaF}_2\text{--LaF}_3$, and $\text{MgF}_2\text{--LaF}_3$ are presented in figures 21–24, in which uncertainty estimates are indicated by the length of the vertical line for each mixture and (ss) = solid solution. Subsolidus relations were inferred from selected X-ray lattice parameter measurements and from microscopic observations.

Table 6.—Bulk compositions before and after thermal analysis for mixtures in the system $\text{CaF}_2\text{--LaF}_3$

Nominal composition, wt pct LaF_3	Calculated ¹ composition, wt pct LaF_3	Difference wt pct LaF_3
20.0	17.3	−2.7
29.0	29.1	+0.1
38.6	37.2	−1.4
52.0	52.0	0
62.6	64.7	+2.1
71.5	74.2	+2.7

¹ Calculated values were derived from lanthanum analyses by X-ray emission techniques. Analytical errors are estimated to be ± 1 pct of the amount present.

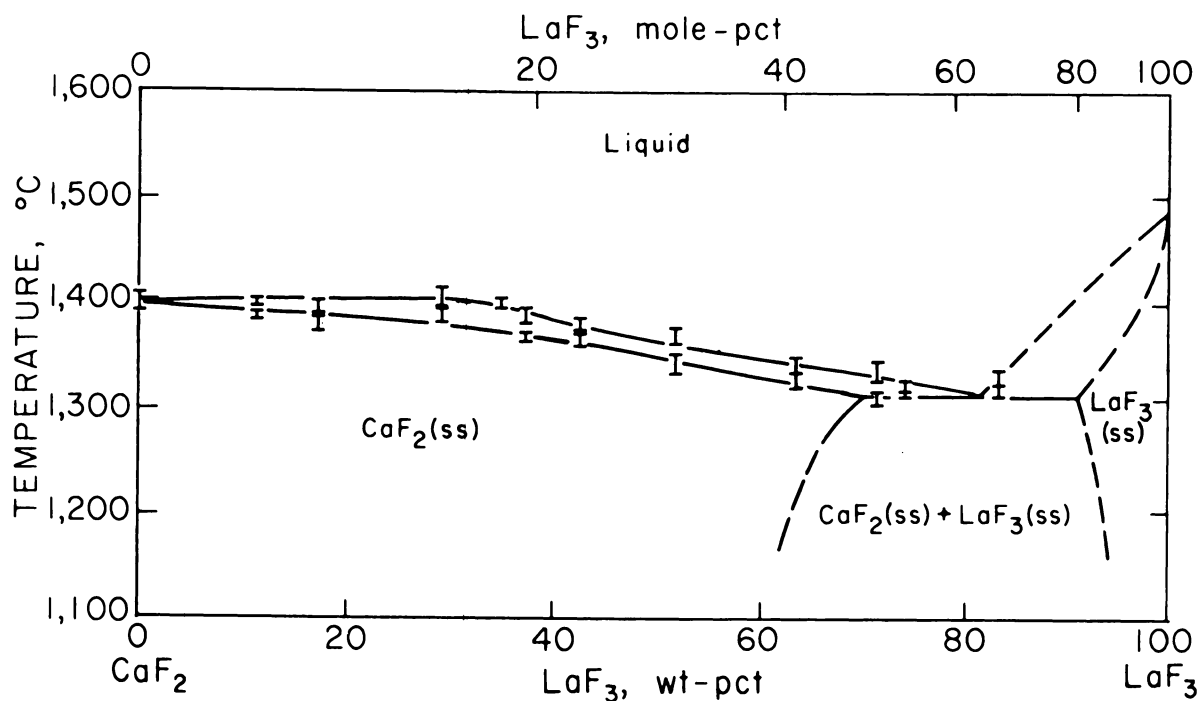


Figure 21.—Liquidus and solidus curves for the system $\text{CaF}_2\text{--LaF}_3$.

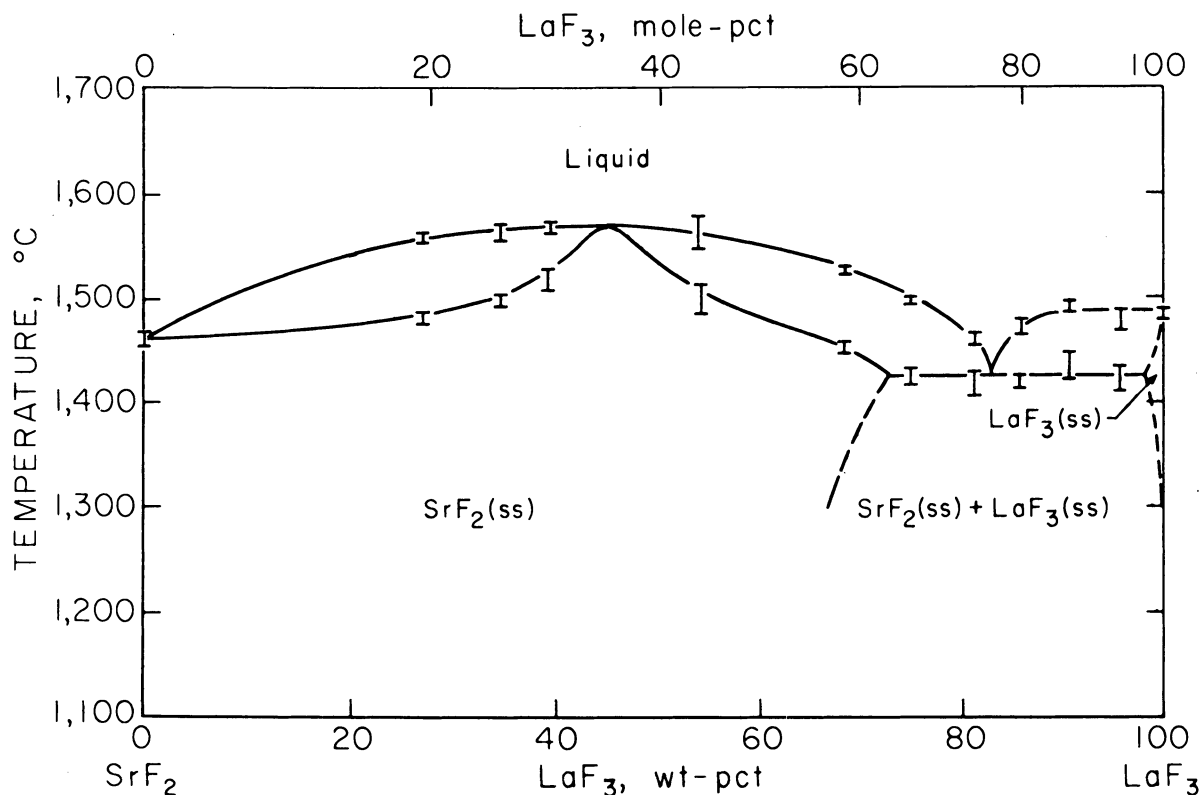


Figure 22.—Liquidus and solidus curves for the system $\text{SrF}_2\text{--LaF}_3$.

No solid solutions were detected by X-ray in the eutectic $\text{MgF}_2\text{--LaF}_3$ system, although minute amounts of both solid solutions must be present. Lattice parameters for MgF_2 and LaF_3 were 4.623 Å (a_0) and 3.051 Å (c_0), and 7.186 Å (a_0) and 7.353 Å (c_0), respectively. Each mixture in this system exhibited a eutectic structure after thermal analysis; the textures of representative compositions are shown in figure 25. The eutectic composition contains 35 ± 1 weight-percent MgF_2 at 1,105° C.

The other systems had similar characteristics, including (1) two solid solutions of the fluorite (CaF_2) and tysonite (LaF_3) structures separated by a solid immiscibility gap and (2) a eutectic. The $\text{SrF}_2\text{--LaF}_3$ and $\text{BaF}_2\text{--LaF}_3$ systems each contain a maximum on the liquidus curve whose temperature is $\sim 110^\circ\text{C}$ and 160°C , respectively, above the melting point of the alkaline-earth fluoride. This maximum is located at compositions where the primary phase is the fluorite solid solution, the LaF_3 solid solution is much

more limited than the fluorite solid solution in each of these systems. No compounds or other intermediate phases were detected in any of the systems studied. In addition, no solid-state transitions were observed in any of the component fluorides in the systems containing LaF_3 . The estimated limits of solid solubility for all terminal solid solutions, determined from the present data, agree to within ± 3 mole-percent of those observed by previous investigators (13-14, 38).

The X-ray data are shown as functions of composition in figure 26 for the systems in which extensive fluorite solid solutions are present. The lattice parameters for these cubic fluorite interstitial solid solutions change linearly with composition. The lattice parameters of mixtures in the $\text{CaF}_2\text{--LaF}_3$ system exhibit the greatest increase with increasing LaF_3 content, whereas parameters in the $\text{SrF}_2\text{--LaF}_3$ system are more independent of compositions. On the other hand, the fluorite lattice parameter in the $\text{BaF}_2\text{--LaF}_3$ system decreases with increasing LaF_3 content.

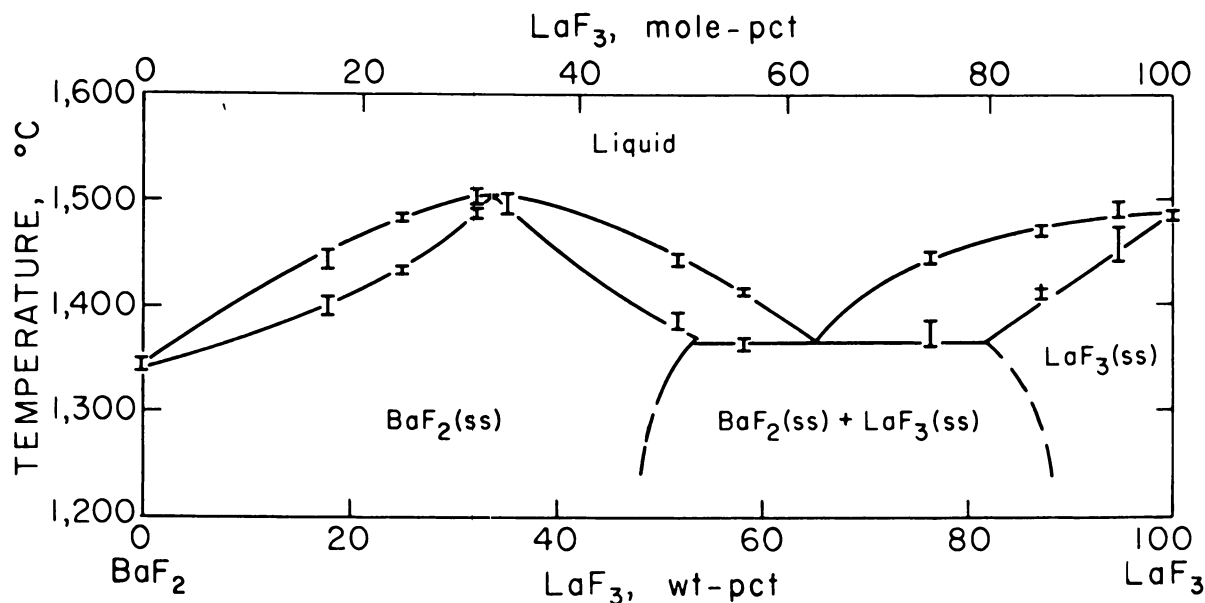


Figure 23. Liquidus and solidus curves for the system $\text{BaF}_2\text{-LaF}_3$.

These observations are consistent with the relative cationic radii (see footnote 4 of this chapter; $\text{LaF}_3 = 1.26$ (1.22) (28, 34) for an La^{3+} coordination number of 8) when the effect of interstitial fluoride ions is considered. On the basis of cationic radii alone, an increase in the lattice parameter of the fluorite solid solution with increasing LaF_3 content would be expected for the system $\text{CaF}_2\text{-LaF}_3$. The observed increase (fig. 26) is also attributed to the additional interstitial F^- ions derived from the substitution of LaF_3 for CaF_2 . In the $\text{SrF}_2\text{-LaF}_3$ system, a decrease in lattice size is expected on the basis of cationic radii alone. The slight increase observed (fig. 26) probably results from the contribution of the interstitial F^- ions. No lattice parameter increase was noted in the $\text{BaF}_2\text{-LaF}_3$ system because the relatively large difference in cationic radii overrides the opposing superimposed effect of the interstitial F^- ions. The solid

solutions based on LaF_3 are less extensive than the fluorite solid solution in these three systems; pertinent lattice parameters are given in table 7.

SYSTEMS CONTAINING YF_3

The presence or absence of intermediate compounds or phases in fluoride flux systems is of particular importance to the electrosag process (23). On the basis of cationic field strengths, which in turn, are a function of cationic size and charge, it is expected that systems containing YF_3 are more likely to form such desirable compounds than corresponding systems containing LaF_3 . In addition, Bacon, Mitchell, and Nishizaki (1) have stated that the most desirable all-fluoride electrosag flux from the standpoint of liquidus temperatures, electrical conductivity, and process stability is $\text{CaF}_2\text{-20 weight-percent } \text{YF}_3$. With this in mind, it appeared desirable to delineate high-temperature phase relations in

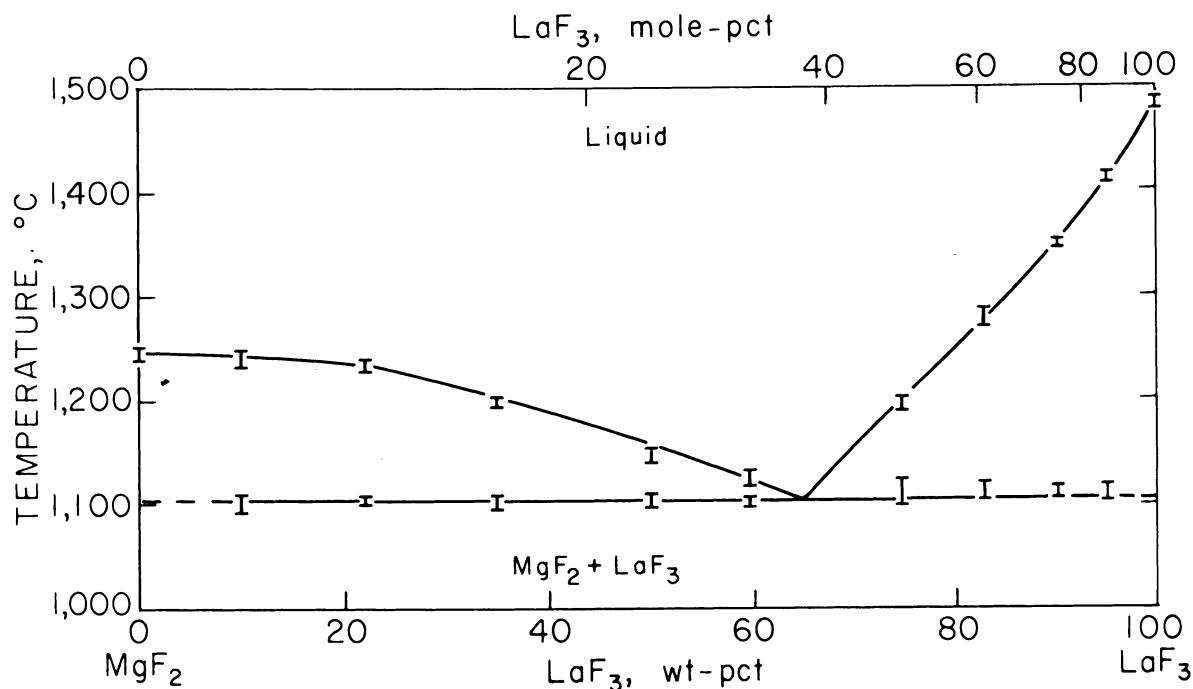
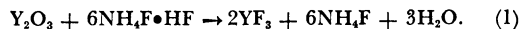


Figure 24.—Liquidus and solidus curves for the system $\text{MgF}_2\text{--LaF}_3$.

systems containing YF_3 which may find application in the electroslag process. Results of such an investigation will permit the comparison of the aforementioned parameters with those in analogous LaF_3 -containing flux systems to determine the most desirable and appropriate classes of fluoride fluxes for use in the electroslag process.

Numerous authors have considered equilibrium relations, densities, and X-ray properties of phases in the $\text{CaF}_2\text{--YF}_3$ system (for example, 8, 12, 29). As a result, the phase diagram of this system is the best known of suitable alkaline-earth fluoride- YF_3 systems. Ippolitov and Maklachko (16) have recently published a diagram of the $\text{BaF}_2\text{--YF}_3$ system. Sobolev, Ippolitov, Zhigarnovskii, and Garashina (30) have studied subliquidus phase compositions in the $\text{CaF}_2\text{--YF}_3$, $\text{SrF}_2\text{--YF}_3$, and $\text{BaF}_2\text{--YF}_3$ systems. However, no temperatures were given. To the authors' knowledge, this is the extent of literature data on alkaline-earth fluoride- YF_3 systems. Therefore, the $\text{SrF}_2\text{--YF}_3$ and $\text{MgF}_2\text{--YF}_3$ systems were selected for study in the present investigation. In addition, the $\text{LaF}_3\text{--YF}_3$ system was studied in order to determine whether suitable compositions for electro-

slag fluxes exist in this rare-earth fluoride- YF_3 system. The experimental techniques used were similar to those described previously in this chapter. However, the YF_3 was synthesized either by (1) hydrate precipitation from a hot aqueous yttrium nitrate solution with 48 percent HF , followed by drying in air of the washed material and decomposition to YF_3 by heating in a stream of hot inert gas (5), or by (2) a slightly modified method from that given by Carlson and Schmidt (5), involving the reaction



A 30 percent excess of $\text{NH}_4\text{F} \cdot \text{HF}$ was used, and the finely ground reactants were heated slowly with constant stirring to approximately 250°C . A thick, pasty mass formed initially with simultaneous copious fuming. After 5 hours of heating, the fuming subsided and the reaction was considered complete. Prior to use, the approximately 25 grams of product were reheated to 600°C for $2\frac{1}{2}$ hours. This YF_3 contained 0.16 to 0.51 percent oxygen; Al, Ca, and Si comprised the bulk of the remaining 0.3 percent impurities. The Y-F atomic ratio of the product averaged 0.34 ± 0.02 .

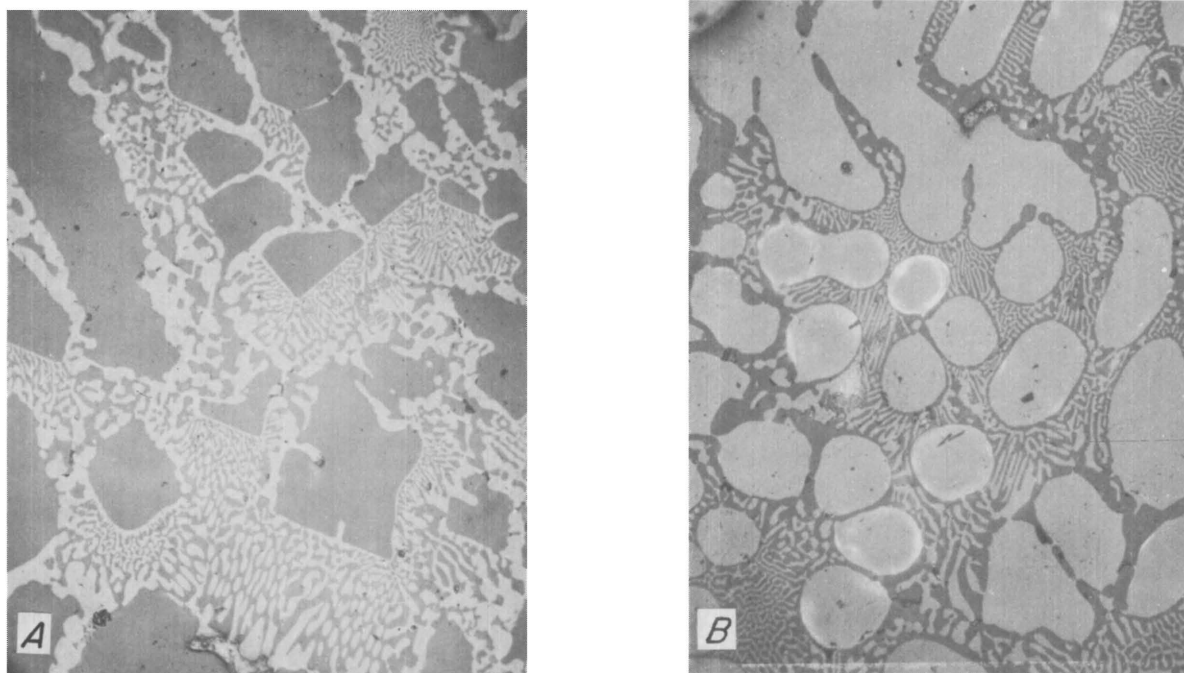


Figure 25.—Compositions in the system MgF_2 – LaF_3 after thermal analysis. *A*, MgF_2 grains (dark areas) in eutectic matrix, 65 wt-pct MgF_2 ; *B*, LaF_3 grains (light areas) in eutectic matrix, 25 wt-pct MgF_2 .

High-temperature phase relations for the LaF_3 – YF_3 , SrF_2 – YF_3 , and MgF_2 – YF_3 systems are presented in figures 27, 28, and 29, respectively. The compositions of the mixtures studied are indicated in each figure. Subliquidus relations were inferred from optical observations as well as room-temperature X-ray powder diffractometry measurements.

LaF_3 – YF_3 System

The LaF_3 – YF_3 system (fig. 27) is characterized by a liquidus curve decreasing from the melting point of LaF_3 ($1,487^\circ \text{C} \pm 2^\circ$) to a eutectic at 81 weight-percent YF_3 and $1,073^\circ \text{C}$. The liquidus curve then increases to the melting point of YF_3 ($1,149^\circ \text{C} \pm 1^\circ$). The melting points of the two components agree well with values reported in the literature, $1,142^\circ \text{C}$ (29) and $1,148^\circ \text{C}$ (25) for YF_3 , and $1,490^\circ \text{C}$ (25) for LaF_3 . An extensive tysonite (hexagonal LaF_3) solid solution is present as well as a restricted cubic (β - YF_3) solid solution. The first-order transition of YF_3 at $1,045^\circ \text{C}$ extends over a considerable portion of the diagram. Evidence for a low-temperature hexagonal compound with a considerable composition range was found, particularly in the DTA determinations. Such a low-temperature com-

pound is believed not to play a significant part in fluxes for the electroslag process and hence was not characterized further.

SrF_2 – YF_3 System

A small maximum on the liquidus curve is present in the SrF_2 – YF_3 system (fig. 28). This occurs at approximately 12 weight-percent YF_3 and 18°C higher than the melting point of SrF_2 , determined to be $1,462^\circ \text{C} \pm 6^\circ$, in agreement with the literature value of $1,463^\circ \text{C}$ (18, 25). Reasons for this have been discussed previously in this chapter. At higher YF_3 contents, the liquidus curve steeply decreases to a eutectic at approximately 55 weight-percent YF_3 and $1,012^\circ \text{C}$. This is similar to the sharp decrease found previously for the CaF_2 – YF_3 system (29). The liquidus curve then increases approximately 100°C as a result of the presence of the compound $\text{SrF}_2 \cdot 2\text{YF}_3$ with hexagonal symmetry whose composition range was estimated from room-temperature X-ray lattice parameter measurements on samples quenched from approximately 900°C . These data are summarized in table 8. With increasing YF_3 contents, the liquidus curve again decreases to an additional eutectic at 98 weight-percent YF_3 and $1,075^\circ \text{C}$ before in-

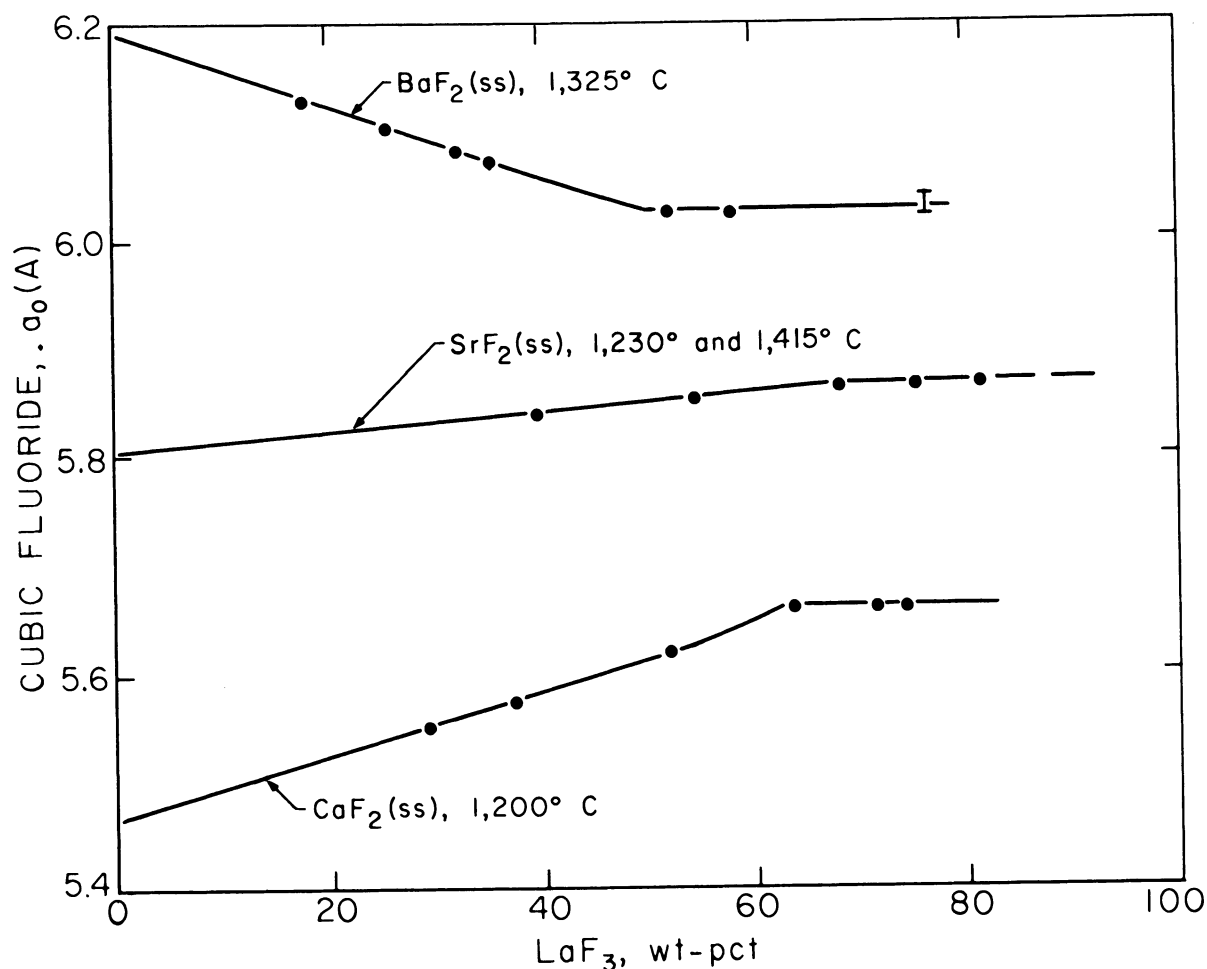
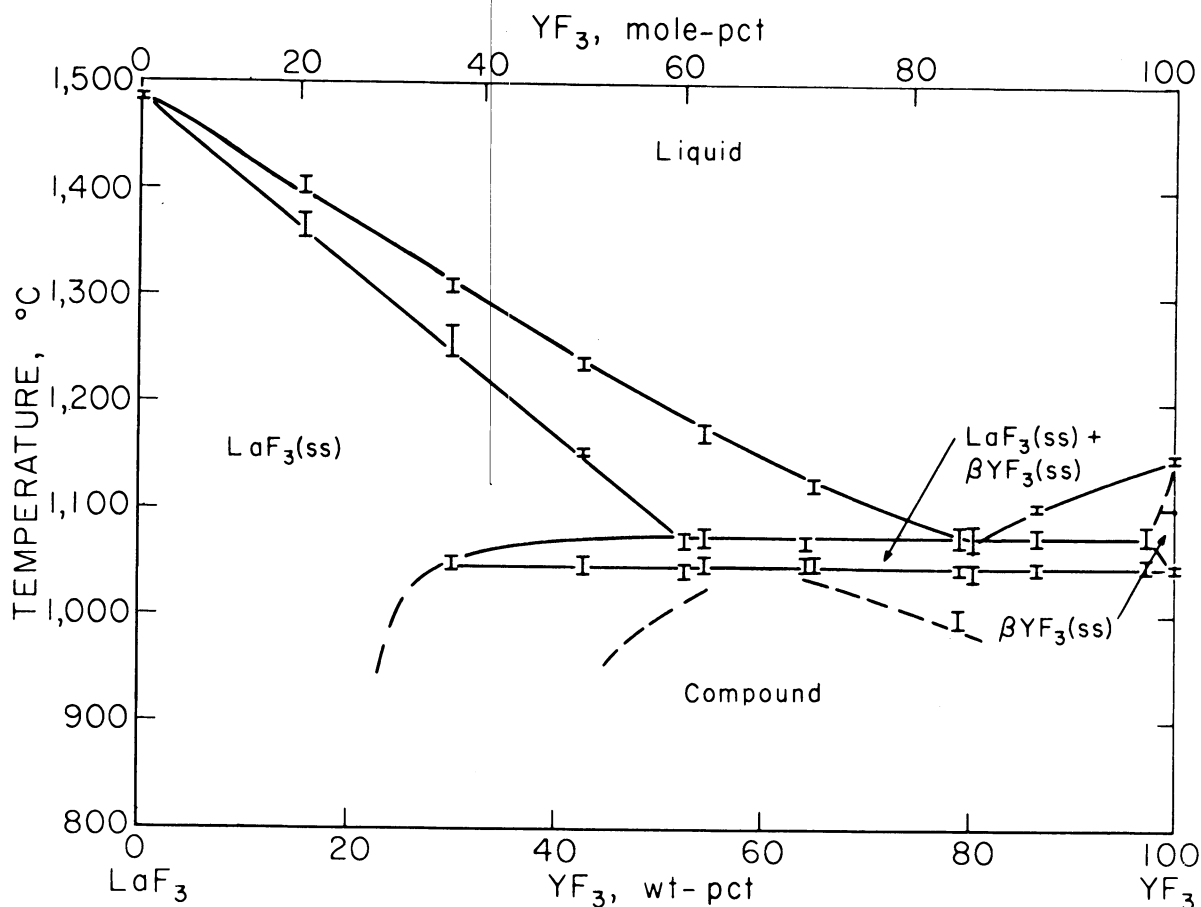


Figure 26.—Variation of lattice parameters as functions of LaF_3 content in the systems $\text{CaF}_2\text{--LaF}_3$, $\text{SrF}_2\text{--LaF}_3$, and $\text{BaF}_2\text{--LaF}_3$.

Table 7.—X-ray lattice parameters for the tysonite phase (LaF_3)¹

Composition (wt-pct LaF_3)	a_0 , Å	c_0 , Å
All systems: 100	7.185 ± 0.005	7.354 ± 0.005
$\text{CaF}_2\text{--LaF}_3$ (1,200°C):		
83.5	7.114 ± 0.005	7.328 ± 0.005
74.2	7.117 ± 0.005	7.323 ± 0.008
71.5	≈ 7.12	≈ 7.26
$\text{SrF}_2\text{--LaF}_3$ (1,230° and 1,415°C):		
95.41	7.18 ± 0.01	7.35 ± 0.02
90.68	7.18 ± 0.01	7.36 ± 0.01
81.4	7.17 ± 0.01	7.37 ± 0.01
75.3	7.17 ± 0.01	7.37 ± 0.01
$\text{BaF}_2\text{--LaF}_3$ (1,325°C):		
94.7	7.205 ± 0.005	7.39 ± 0.01
87.5	7.249 ± 0.007	7.417 ± 0.007
76.5	7.269 ± 0.005	7.428 ± 0.005
58.1	7.24 ± 0.01	7.41 ± 0.01

¹ Determined at room temperature on samples quenched from temperature(s) indicated.

Figure 27.—The System $\text{LaF}_3\text{--YF}_3$.

creasing to the YF_3 melting point. The first-order transition of YF_3 at $1,045^\circ\text{C}$ was evident in only two compositions (99.3 and 100 weight-percent YF_3). Little or no SrF_2 is soluble in YF_3 at sub-liquidus temperatures. However, a relatively large cubic fluorite solid solution field exists.

$\text{MgF}_2\text{--YF}_3$ System

The system $\text{MgF}_2\text{--YF}_3$ (fig. 29) is of the simple eutectic type with a very small amount of orthorhombic ($\alpha\text{-YF}_3$) solid solution and perhaps a limited amount of YF_3 solid solubility in MgF_2 . The high-temperature cubic form of YF_3 (β) occupies a very small stability area. Indications of a low-temperature compound, as shown in figure 29, were present in several compositions. A typical photomicrograph of phases present in this system is shown in figure 30. Our MgF_2 was found to melt at $1,246^\circ\text{C} \pm 4^\circ$, in agreement

with literature values of $1,251^\circ\text{C}$ (18) and $1,252^\circ\text{C} \pm 5^\circ$ (26).

When YF_3 instead of LaF_3 is added to cubic alkaline-earth fluorides, the resulting systems exhibit (1) a less-pronounced liquidus maximum at low trifluoride contents, (2) two eutectics as a result of the formation of a stable compound over a composition range, (3) one more-restricted solid solution instead of two, (4) lower liquidus temperatures, and (5) a solid phase transition. These observations can be attributed to the smaller cationic radius of Y^{3+} compared to La^{3+} . This increases the difference in radii between the trivalent cation and a given divalent alkaline-earth cation and thus causes more limited solid solution in YF_3 -containing systems. In addition, there is a greater difference in ionic field strengths in alkaline-earth fluoride systems containing YF_3 than in analogous systems containing

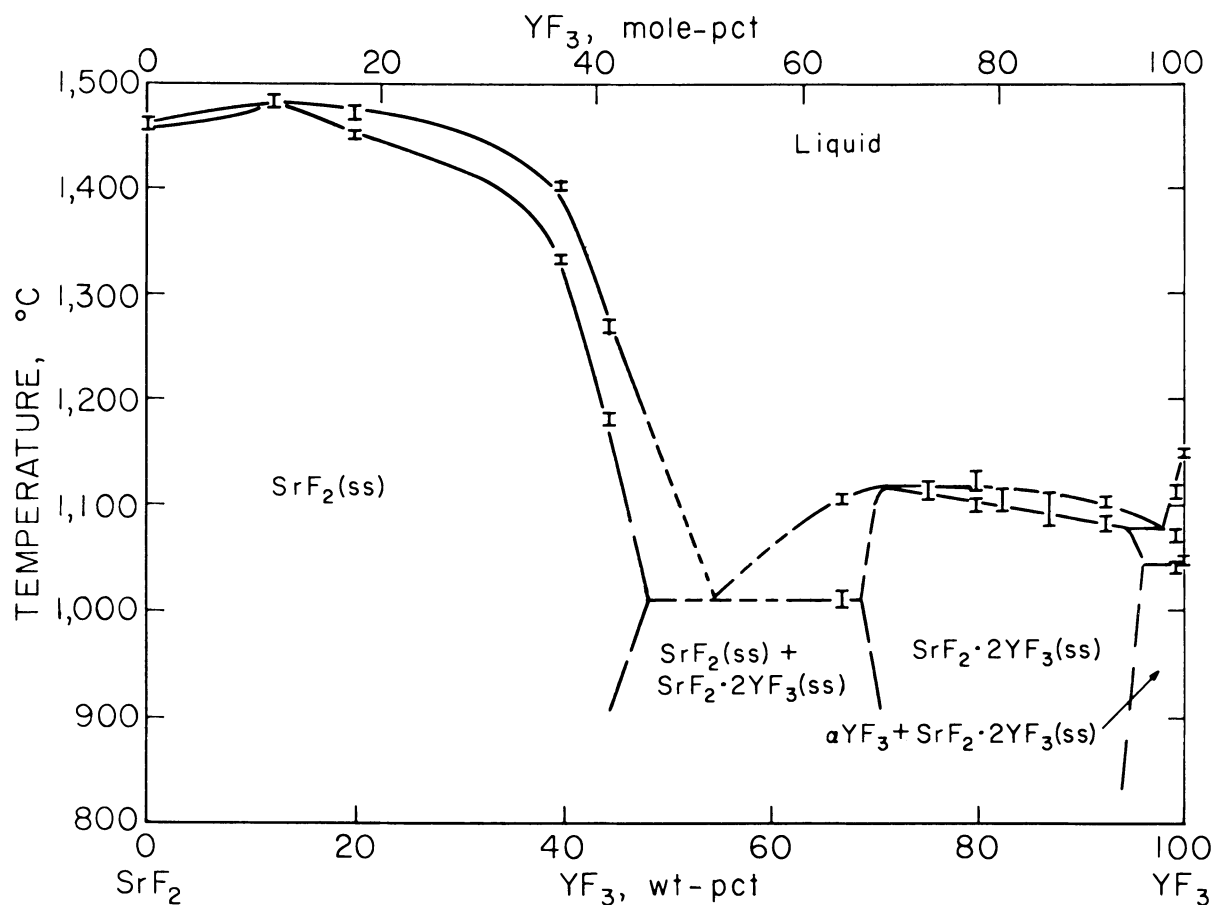
Figure 28.—The System $\text{SrF}_2\text{--YF}_3$.

Table 8.—Room-temperature X-ray lattice parameters of the hexagonal compound in the system $\text{SrF}_2\text{--YF}_3$ on samples quenched from $\sim 900^\circ\text{C}$ ¹

Bulk composition, wt-pct SrF_2	a_o , Å	c_o , Å
7.6	6.856 ± 0.005	7.03 ± 0.01
13.2	6.882 ± 0.001	7.025 ± 0.001
17.5	6.884 ± 0.004	7.031 ± 0.004
20.2	6.898 ± 0.001	7.042 ± 0.001
24.7	6.914 ± 0.005	7.054 ± 0.005
33.0	6.916 ± 0.005	7.056 ± 0.005

¹ Insufficient amounts of this phase were present to obtain meaningful lattice parameter measurements in mixtures whose bulk compositions were 0.9 and 55.7 wt-pct SrF_2 .

LaF_3 . This manifests itself not only in more limited or absent solid solutions but also in the formation of compounds or intermediate phases

which do not exist in corresponding systems containing LaF_3 . The existence of a first-order solid phase transition and lower liquidus temperatures in YF_3 systems is attributed directly to YF_3 , whose melting temperature is more than 300°C lower than that of LaF_3 . Furthermore, LaF_3 possesses no such solid-state transition. In comparing the systems $\text{MgF}_2\text{--YF}_3$ and $\text{MgF}_2\text{--LaF}_3$, similar differences are noted. Such differences, due to dissimilarities in the properties of YF_3 and LaF_3 , can be postulated from figure 27.

PHYSICOCHEMICAL AND THERMODYNAMIC PROPERTIES OF FLUORIDE FLUXES

Observations over a period of years have provided convincing evidence that the physicochemical properties of the fluxes are of prime importance in establishing successful electroslag

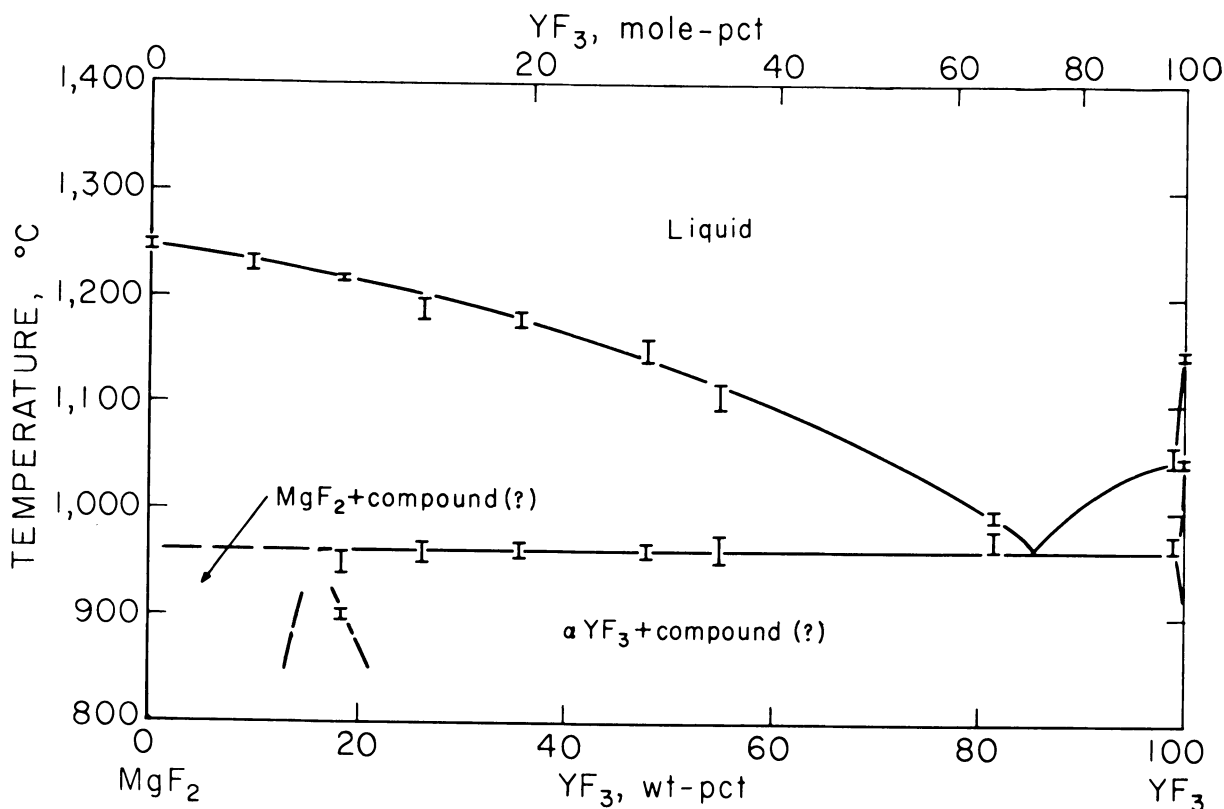


Figure 29.—The System $\text{MgF}_2\text{--YF}_3$.

melting operations. In addition, a knowledge of the thermodynamic properties of molten fluxes provides intelligent guidelines for determining high-temperature flux stabilities which aid in optimizing suitable electroslag melting fluxes. Optimum properties of an ideal flux in addition to those mentioned earlier in this chapter include (1) the heat of fusion of the flux should be low enough for easy melting, (2) a low thermal conductivity should provide an insulating cap on the ingot, (3) the viscosity should be sufficiently low to promote effective stirring for gas removal at the slag-gas interface, yet high enough for maximum metal droplet exposure for maximum possible refining, (4) the flux should possess a low vapor pressure at the high temperatures obtained during the electroslag process (this requires a low oxygen fugacity in the flux with transition metal oxides unacceptable due to undesirable oxygen transfer from flux to metal), (5) the flux should possess as high a surface tension as possible, (6) the flux should possess a relatively large solidification range (liquidus-

solidus temperature interval) for optimizing ingot surfaces, (7) the flux should be stable at high temperatures and be compatible with the metal to be melted at such temperatures (this means the high-temperature free energy of formation should have as low a negative value as possible), and (8) the primary flux phase should possess a melting point higher than that of the metal to permit a solid slag skin to form between the ingot and mold during melting. This skin is responsible for smooth, workable ingot surfaces.

Optimum physical properties of fluxes have largely been determined empirically by observation of process characteristics. One important parameter is the process operating temperature, which is usually measured in the slag bath between the electrode tip and the molten metal pool. Flux compositions with determined low vapor pressures at process operating temperatures are therefore required. High-temperature flux densities (determined experimentally) must of course be lower than those of the metal or alloy

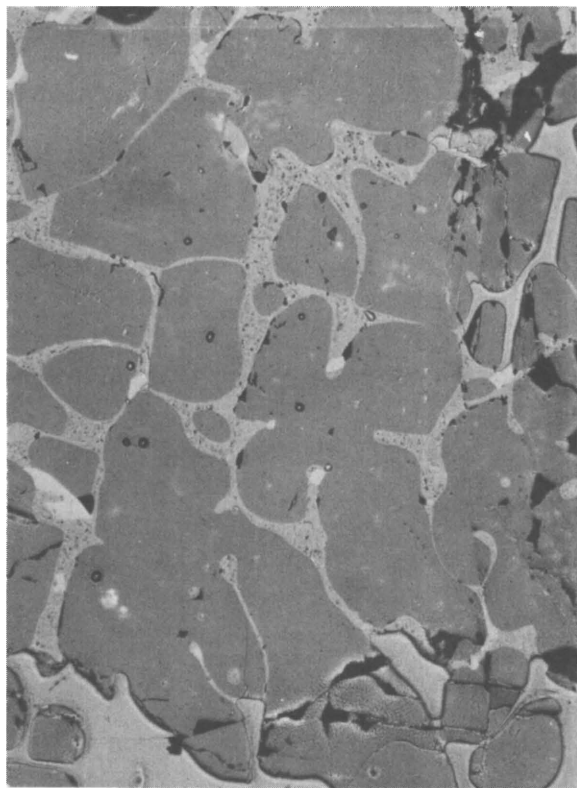


Figure 30.—Microstructure of 81.5 wt-pct MgF_2 - YF_3 composition after thermal analysis. Primary dark MgF_2 grains in a eutectic matrix containing MgF_2 , YF_3 (light-gray), and a third phase (most reflective) believed to be a low-temperature compound.

to be melted. Experimental determination of the physical properties such as electrical conductivity and viscosity of common fluxes are required in order to evaluate the optimum values for use in electroslag melting.

Available literature data for important physical properties of some appropriate fluoride flux compounds as well as representative reactive metals are shown in table 9. High-temperature densities are presented in table 10. Note that all of the listed compositions possess melting points below that of the reactive metals listed. This is also true of the high-temperature densities with the exception of LaF_3 as applied to titanium. (Therefore, LaF_3 is unsuitable for electroslag melting of this metal.) The heats of fusion values of all of the listed compositions lie within what are considered acceptable ranges. The standard free energies of formation of these fluorides are

low enough to preclude reactions which form compounds with titanium, for which thermodynamic data are available at 2,000 K as shown in table 5.

Physicochemical data become more scanty when binary fluoride systems are considered. The high-temperature densities for all mixtures in the BaF_2 - SrF_2 system are greater than that for CaF_2 , but less than that for molten reactive metals above their melting points (17). At 1,727° C, viscosities in this flux system may be slightly greater than those for CaF_2 , whereas stabilities and thermal conductivity values are approximately equal. As seen in table 9, the heats of fusion for the pure components, BaF_2 and SrF_2 , are less than those for CaF_2 . Fluxes in the BaF_2 - SrF_2 system would, therefore, require less power for melting than an equal quantity of CaF_2 . The lower power requirement (excluding overall power consumption) may partly offset the higher cost of BaF_2 - SrF_2 slags.

Data on high-temperature electrical conductivities are sparse for fluoride systems. Bacon, Mitchell, and Nishizaki (1) determined the electrical conductivity of molten CaF_2 - LaF_3 fluxes; with LaF_3 additions up to 20 weight-percent, the specific conductivity at 1,500° to 1,600° C decreased significantly. These workers concluded that this behavior prevents arcing by causing insufficient power density and melt rate in the electroslag process.

THERMODYNAMIC OBSERVATIONS

The determined minimum on the liquidus curve of the BaF_2 - SrF_2 system indicates that the heat of mixing for the solid solution is greater than that for the liquid phase. A greater positive deviation from ideality would be expected for the solid than for the liquid solution.

Since no solid solutions, compounds, or intermediate phases were observed in the MgF_2 - LaF_3 system, the high-temperature thermodynamic properties of the liquid phase can be estimated (19). The heat of fusion for MgF_2 was taken as 13,900 cal mole⁻¹ $\pm$ 200 (table 10), and that for LaF_3 was estimated from the liquidus data in figures 21-24 and phase diagram theory as 14,500 cal mole⁻¹. At the melting point of titanium (1,948 K $\pm$ 7), the calculated activities of each component in the composition range where it is the primary phase show nearly ideal relations. The activities of the components over the remainder of the system were calculated from a binary integration of the Gibbs-Duhem equation

Table 9.—Selected properties of materials for electroslag melting ¹

Material	mp, °C	bp, °C	ΔH_{fusion} , kcal mole ⁻¹	ΔG° at 2,000 K, kcal mole ⁻¹	Vapor pressure at 2,000 K, (log. atm)	Electrical conductivity, ohm ⁻¹ cm ⁻¹	Viscosity, poises	Thermal conductivity, 10 ⁻³ cal sec ⁻¹ cm ⁻¹ °C ⁻¹
MgF ₂	1,246	2,227 (35)	13.9 (35)	-172 (10)	-1.66 (19)	NA	NA	NA
CaF ₂	1,423	~2,500 (32)	6.8 (35)	-210 (10)	-2.41 (19)	6.39 at 1,527° C (7)	0.058 at 1,600° C (1)	24 (2)
SrF ₂	1,462	2,477 (35)	4.3 (35)	-210 (10)	-2.27 (19)	NA	NA	NA
BaF ₂	1,346	2,200 (35)	3.0 (35)	-214 (10)	-1.61 (19)	NA	NA	27 (2)
YF ₃	1,149	2,227 (9)	13.0 (9)	-300 (10)	NA	NA	NA	NA
LaF ₃	1,487	2,327 (9)	14.5	-315 (10)	-2.40 (19)	3.36 at 1,650° C (24)	NA	NA
Titanium ..	1,675 (32)	3,285 (19)	4.5 (19)	NAP	-3.92 (19)	NA	NA	NA
Zirconium ..	1,815 (22)	4,400 (19)	4.6 (19)	NAP	-9.34 (19)	NA	0.058 at 1,527° C (7)	NA
Vanadium ..	1,910 (22)	~3,350 (19)	NA	NAP	-6.36 (19)	NA		24 (2)

NA Not available. NAP Not applicable.

¹ Italicized numbers in parentheses refer to references at the end of this chapter. Data obtained from work presented in this chapter are not referenced.

Table 10.—Densities of molten fluorides at or slightly above melting points of reactive metals¹

Metal	Titanium	Zirconium	Vanadium
Temperature °C	1,675	1,835	1,930–1,940
Density (g-cm ⁻³) of—			
Metal	4.11	6.06	5.734
CaF ₂	2.417	2.358	2.319
SrF ₂	3.33	3.23	3.126
BaF ₂	3.824	<3.75	<3.75
MgF ₂	2.213	2.133	<2.125
LaF ₃	4.462	4.357	4.29

¹ Data were taken from references 17 and 22. Temperature given is that at which the density of the metal was determined; the fluoride densities were interpolated or extrapolated from data in the literature.

using the α -function (6). These activities exhibit slightly negative deviations from ideality. The activity versus composition data permit calculation of the free energy of mixing (ΔG^m) in kcal mole⁻¹ according to the equation

$$\Delta G^m = RT \frac{(N_{\text{MgF}_2} \ln a_{\text{MgF}_2} + N_{\text{LaF}_3} \ln a_{\text{LaF}_3})}{1,000} \quad (2)$$

where R is the gas constant (1.987 cal deg⁻¹ mole⁻¹), T is the melting point of titanium, and a and N are the activities and mole fractions, respectively. When these data are plotted versus composition, ΔG^m is an almost symmetrical function of composition, indicating simple solution behavior for this system at temperatures of interest in electroslag melting.

In the absence of specific determinations of component activities (for example, by vapor pressure measurements or emf cells) very little can be said definitely concerning the high-temperature activities in the liquid phase of the systems CaF₂–LaF₃, SrF₂–LaF₃, and BaF₂–LaF₃. In each system, the heats of mixing of the solid-solution phases are greater than those for the liquid phases. The heats of mixing for both phases in each system are greater than zero.

FURTHER APPLICATIONS TO THE ELECTROSLAG PROCESS

Although no high-melting-point compounds were detected in any of the systems studied, significant maxima on the liquidus curves were observed in two of the systems. These dystectics are believed to result from the aforementioned substitution of interstitial fluoride ions into the fluorite solid solution. This substitution introduces defects into the crystal structure, resulting in a less-than-normal entropy of fusion because of the added disorder. This effect increases the

ratio of the heat of fusion to the entropy of fusion and thus increases the liquidus temperature (29).

In the system SrF₂–LaF₃, the dystectic temperature is only $\approx 100^\circ$ C lower than the melting point of titanium. This interval is the smallest between the liquidus temperature of a flux and the melting point of a reactive metal observed in any fluoride system thus far; hence, this dystectic represents a desirable flux composition for the melting of titanium. The liquidus maximum in the BaF₂–LaF₃ system occurs at a temperature slightly higher than the LaF₃ melting point. In addition, the flux density of the BaF₂–LaF₃ dystectic is expected (on the basis of a linear interpolation between the fluoride components in each system as a first approximation) to be lower than that of titanium at its melting point. The approximate compositions where flux densities at the melting point of titanium become larger than the density of the metal are 48, 71, 83, and 84 weight-percent LaF₃ for the BaF₂–LaF₃, SrF₂–LaF₃, CaF₂–LaF₃, and MgF₂–LaF₃ systems, respectively. Therefore, flux compositions which contain more than these amounts of LaF₃ are unsuitable for electroslag melting of titanium. All flux compositions in these systems are less dense than zirconium and vanadium at temperatures above their respective melting points, as indicated in table 11. Fluxes containing YF₃ can be used if the YF₃ content remains less than approximately 40 weight-percent in order to maintain liquidus temperature sufficiently high to produce reasonably smooth ingot surfaces. Despite the existence of compounds or intermediate phases at higher YF₃ concentrations, which increase liquidus temperatures in all cubic alkaline-earth fluoride–YF₃ systems (16, 29), the absolute liquidus temperatures are insufficiently high to be of significance when applied to electroslag melting. Analogous systems with LaF₃ substituted for YF₃ are better candidates for electroslag fluxes at high bulk trivalent fluoride contents, provided flux densities are taken into account as noted earlier in this chapter. This is because of their higher liquidus temperatures, despite the fact that no compounds or intermediate phases are present in these systems. On the other hand, a 20 weight-percent YF₃–CaF₂ flux has a slightly higher liquidus temperature and slightly lower electrical conductivity at 1,500° C than a 20 weight-percent LaF₃–CaF₂ flux (see above and references 1 and 16); therefore, for electroslag melting applications, selected fluxes

containing YF_3 may be preferred over similar fluxes containing LaF_3 . This comparison may be valid for YF_3 - and LaF_3 -containing systems with other alkaline-earth fluorides, although reliable electrical conductivity measurements are not available.

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CHAPTER 6.—OXIDE-FLUORIDE FLUX SYSTEMS FOR ELECTROSLAG MELTING¹

By R. H. Nafziger

A cursory examination of several compilations of oxide-fluoride phase diagrams reveals a vast amount of information. However, compositions in relatively few of these systems are suitable for use as fluxes in the electroslag process. Criteria for the fluoride components are outlined in chapter 5. Oxide components of electroslag flux systems should be selected on the basis of similar properties. Among these are (1) high stability with respect to the temperatures involved and the metal to be melted, (2) relatively low cost, (3) high refining capabilities, (4) low toxicity, and (5) single valency cations. These requirements confine suitable oxide components to alkaline-earth oxides, sesquioxides, and possibly group IV oxides.

This chapter discusses liquidus temperatures, melting ranges, primary crystalline phases, and available physicochemical properties of important binary, ternary, quaternary, and higher order oxide-fluoride flux systems for use in the electroslag process. Relatively uncommon specialty fluxes are also described.

It should be remembered that the selection of electroslag fluxes invariably involves compromises which depend on the objectives of the melting and ingot qualities desired.

BINARY OXYFLUORIDE SYSTEMS

$\text{CaF}_2\text{—CaO}$

When electroslag process technology was in its infancy, fluxes in this system were used to electroslag-melt a wide variety of low- and high-carbon steels, stainless steels, and iron. Such fluxes must be fused prior to use in order to avoid lime hydrolysis which contributes to ingot porosity and cracking. Typical flux compositions include (in weight-percent) 70 CaF_2 –30 CaO , 80 CaF_2 –20 CaO (ANF-7; W1A) and 95 CaF_2 –

5 CaO (ANF-1P; X5AA)². It can be seen from figure 31 that suitable electroslag flux compositions in this system must contain at least 60 weight-percent CaF_2 .

Although there is some disagreement regarding the position of eutectic and the hypoeutectic liquidus temperatures, the system is considered a simple binary eutectic type in all available literature sources, nearly all of which are based on thermal analysis determinations (1, 6, 16, 25–27, 37, 50, 58). A composite phase equilibrium diagram is presented in figure 31. The eutectic temperature is 1,360° C, and the eutectic composition is approximately 80 to 86 weight-percent CaF_2 . While conducting electrical resistivity measurements, Bääk (1) discovered a liquid immiscibility region (fig. 31). Korpachev, Sryvalin, and Burylev (27) also reported this phenomenon. Other authors (6, 16, 25–26, 37, 50, 58), however, failed to detect any evidence of two liquids. Zhmoldin and Chatterdshi (58) attributed the alleged immiscibility to the presence of non-equilibrium crystalline CaO . The presence of the liquid immiscibility region also dictates a steep liquidus curve at compositions greater than 99.5 weight-percent CaF_2 , which is thermodynamically improbable (26). Diagrams showing the melting point of CaF_2 to be ~1,380° to 1,390° C are not regarded as accurate due to impurities present. As mentioned previously, there exist discrepancies among different investigators with regard to the hypoeutectic liquidus curves. From a strictly equilibrium standpoint, the steep convex-upward curves of Zhmoldin and Chatterdshi (58) and Kor and Richardson (26) are considered most plausible. However, the less steep curves at lower temperatures are likely to be more applicable to electroslag fluxes (which may not represent true equilibrium and/or may contain impurities). Since the common 80 CaF_2 –20 CaO flux has

¹ Adapted in part from High-Temperature Science, v. 5, 1973, pp. 414–422; J. Metals, v. 25, November 1973, pp. 55–61.

² The first item in each set of parentheses, is the Soviet designation; the second item is the designation given by Bhat (2).

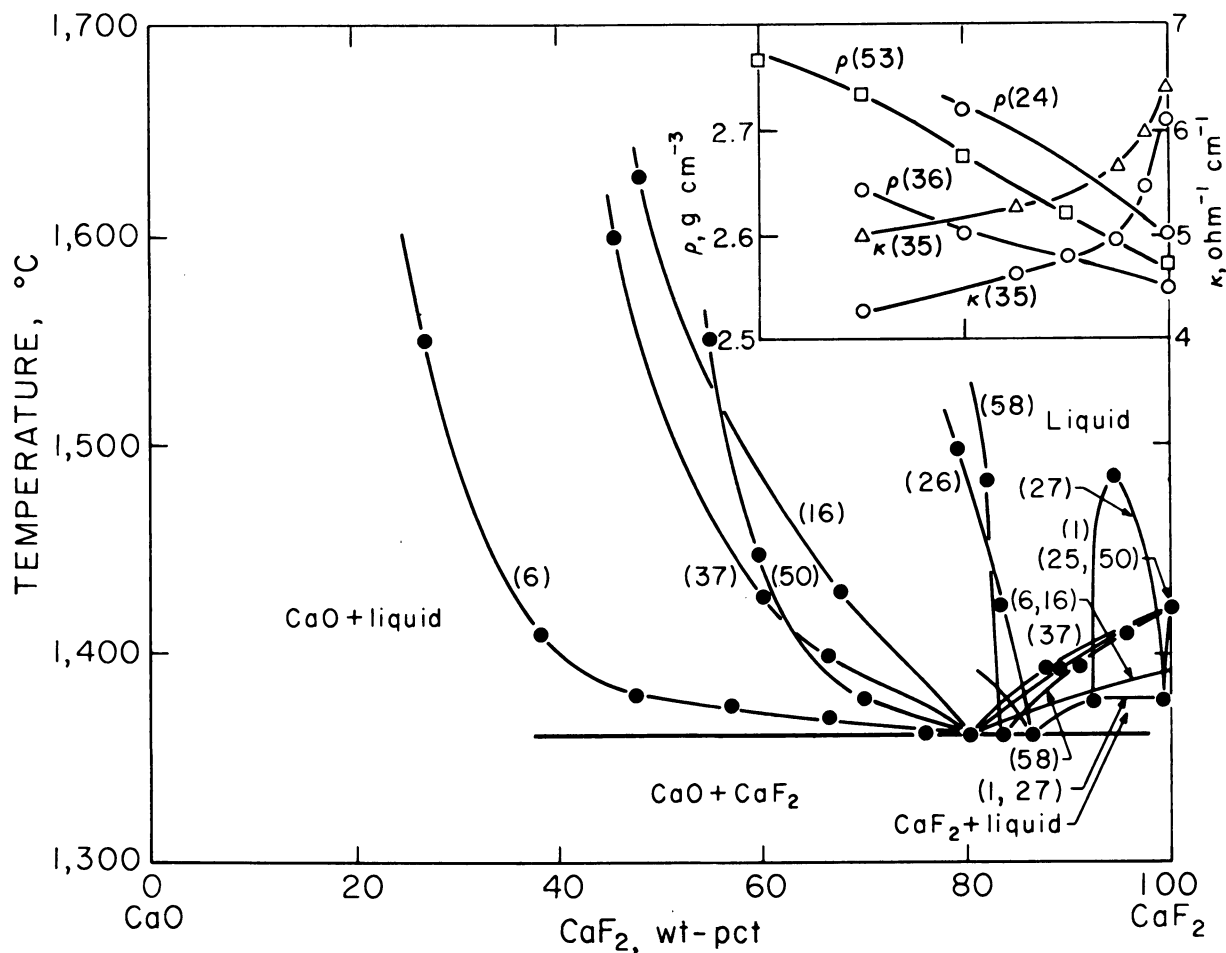


Figure 31.—The system CaO-CaF_2 . Numbers on the liquidus and physical property curves refer to references at the end of this chapter. Symbols for temperatures of the physicochemical property curves are $\square = 1,400^\circ \text{C}$, $\circ = 1,500^\circ \text{C}$, and $\triangle = 1,600^\circ \text{C}$.

been successfully used to electroslag-melt steels, a liquidus temperature of $1,500^\circ$ to $1,600^\circ \text{C}$ as implied by the steeper curves could not be applicable.

Important physicochemical properties of molten $\text{CaF}_2\text{-CaO}$ fluxes are shown in figure 31 with the same abscissa scale as that given for the phase diagram. With increasing CaF_2 contents, the specific electrical conductivity (κ) increases and the density (ρ) decreases. Differences in density values at $1,500^\circ \text{C}$ are noted between references 36 and 24. However, in all cases, the densities are considerably less than those of common electroslag-melted metals, which is a prerequisite for a good electroslag flux. Zhmoidin (56) reported specific conductivity values ranging from $6.52 \text{ ohm}^{-1}\text{cm}^{-1}$ at 60 weight-percent CaF_2 at $1,600^\circ \text{C}$. These values are considerably greater

than those determined by Mitchell and Cameron (35) and plotted in figure 31. Klyuev and Kablukovskii (24) have shown that the surface tension of molten $\text{CaF}_2\text{-CaO}$ fluxes decreases from 364 erg cm^{-2} at 80 weight-percent CaF_2 to 256 erg cm^{-2} for pure CaF_2 at $1,500^\circ \text{C}$.

Davies and Wright (12) have measured viscosities in molten CaO-CaF_2 fluxes using the rotating crucible principle. At $1,500^\circ \text{C}$, viscosities decreased from 0.095 poise at 80 weight-percent CaF_2 to 0.03 poise at 85 weight-percent CaF_2 , with an increase to 0.067 poise for pure CaF_2 . These fluctuations correlate most closely with the liquidus temperatures given by Kor and Richardson (26) and Zhmoidin and Chatterdzhi (58). High flux viscosities promote small metal droplet size, longer droplet residence times in the flux, minimal stirring action, and increases of non-

metallic inclusions in ingots prepared by the electroslag process.

Fluxes in the $\text{CaO}-\text{CaF}_2$ system are used primarily for their desulfurization capacity, with a minimal contribution of nonmetallic oxide inclusions to the metal. The lower cost of these fluxes compared with that of other binary oxy-fluoride systems is also a factor in their use (14).

$\text{CaF}_2-\text{Al}_2\text{O}_3$

Although this system is not strictly binary, it is perhaps the most widely used two-component system for electroslag melting a variety of ferrous alloys. Suitable compositions usually contain less than 40 weight-percent Al_2O_3 to avoid unreasonably high liquidus temperatures (fig. 32). The early work of Pascal (43) placed the eutectic

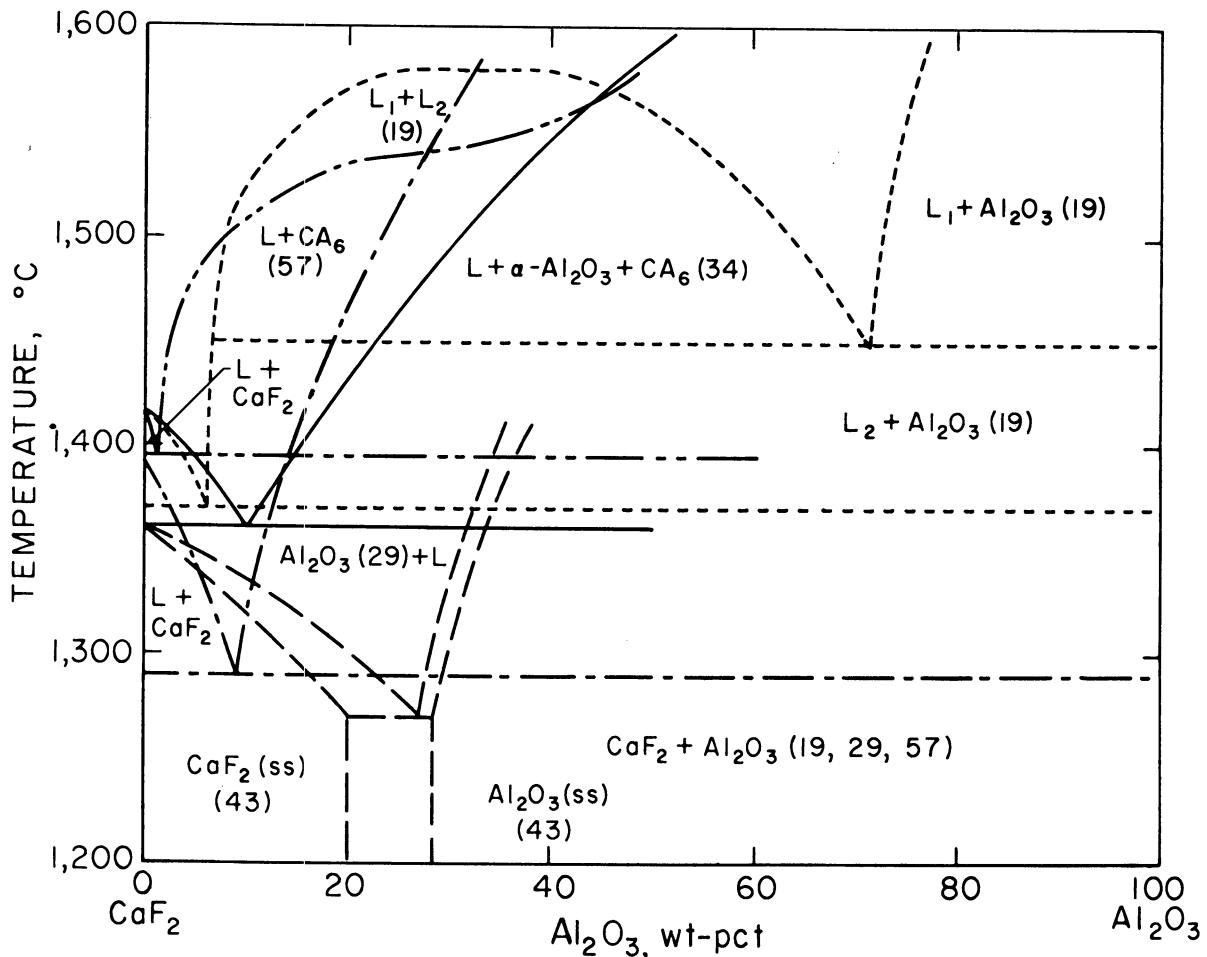
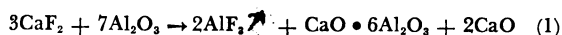


Figure 32.—The system $\text{CaF}_2-\text{Al}_2\text{O}_3$. Solid curves are from reference 34, dashed curves from 43, dot-dashed curves from 29, double dot-dashed curves from 57, and dotted curves from 19. Numbers following phase designations refer to references at the end of this chapter. Further abbreviations are L = liquid (with subscripts denoting two liquids), ss = solid solution, and $\text{CA}_6 = \text{CaO} \cdot 6\text{Al}_2\text{O}_3$.

composition near 30 weight-percent Al_2O_3 . On this basis, this composition has become the most commonly used electroslag flux in this system [ANF-6, Soviet designation; and ZIA as designated by Bhat (2)].

The CaF_2 - Al_2O_3 phase diagrams which have been published are shown superimposed in figure 32. The variety of eutectic compositions and temperatures is presumably due to the different determinative methods and the quality of materials used. Pascal (43) gives the lowest temperatures and postulated considerable solid solubility of Al_2O_3 in CaF_2 . The relatively low temperatures and high Al_2O_3 content of the eutectic are probably due to impurities (chiefly CaO) in the CaF_2 . As will be seen later, the CaF_2 - Al_2O_3 boundary curve in the CaF_2 - CaO - Al_2O_3 system becomes more oxide-rich as the CaO content increases. Pascal's diagram is most applicable to commonly used commercial CaF_2 - Al_2O_3 electroslag fluxes, since these inevitably contain several percent CaO arising either from the hydrolysis of CaF_2 in air or from the irreversible reciprocal reaction of CaF_2 and Al_2O_3 which forms volatile AlF_3 . Kuo and Yen (29) and Mitchell and Burel (34) conducted their investigation in an inert atmosphere, and thus minimized hydrolysis and CaO formation. These authors obtained essentially identical eutectic compositions. The difference in eutectic temperatures is believed due to the different experimental methods used. The liquid phase persists to lower temperatures when sample quenching is employed (29). The presence of calcium hexaluminate ($\text{CaO} \cdot 6\text{Al}_2\text{O}_3$) noted by Mitchell and Burel (34) probably results from a secondary reaction of the type



in a dry, inert atmosphere. Varying amounts of formed $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ could account for liquidus temperature variations in relatively high-bulk Al_2O_3 compositions.

When CaF_2 - Al_2O_3 mixtures are heated in sealed capsules (closed conditions), relatively high liquidus temperatures (for example, $1,540^\circ$ to $1,580^\circ$ C for 70CaF_2 - $30\text{Al}_2\text{O}_3$) with liquid immiscibility or a tendency thereto (implying positive thermodynamic deviation from ideality and large Raoultian activities of CaF_2 and Al_2O_3) are obtained (19, 57). However, the calcium hexaluminate phase persists and the eutectic compositions are higher in CaF_2 because of very low CaO contents. The higher temperatures are perhaps caused by higher than atmospheric pres-

ures developed in the sealed capsules as a result of the formation of AlF_3 according to reaction 1 (57). In any case, sealed-capsule experiments are not directly applicable to the electroslag process and are noted here only for comparison purposes. In all investigations, no additional compounds other than those involving CaO have been reported. With the exception of Pascal's early work (43), no evidence of solid solubility was noted.

Electrical conductivity measurements of liquid CaF_2 - Al_2O_3 fluxes show a larger decrease with Al_2O_3 additions than with equivalent amounts of CaO additions. (Compare figures 31 and 33). At lower temperatures, where conductivity values are lower, this decrease is less pronounced. The significant decrease has been attributed to the formation of AlOF_2^- and $\text{AlO}_2\text{F}_2^{3-}$ complexes which remove the F^- contribution to the overall ionic mobility (35). Figure 33 presents representative electrical conductivity determinations at the temperature of interest to the electroslag process. The lower values for CaF_2 given by Zhmoidin (56) and Evseev (17) can be attributed to CaO impurities, as can the higher values given by these authors for CaF_2 - Al_2O_3 melts.

As noted in figure 33, flux densities increase as Al_2O_3 is added to CaF_2 and as temperatures decrease. The increase in density is due to the smaller ionic radius of Al^{3+} (and hence greater binding energy and packing) compared with Ca^{2+} . The only discrepancy in the data is that at $1,600^\circ$ C between Mitchell and Joshi (36) and Stepanov and Lopaev (53). This is attributed (57) to the selective absorption of the components by the graphite crucibles used by Stepanov and Lopaev.

Viscosities of molten CaF_2 - Al_2O_3 fluxes increase in proportion to the Al_2O_3 content with very little difference noted as a function of temperature (fig. 33) (12, 55). As expected, the viscosities are greater for a given composition for temperatures at which a solid phase is present ($1,400^\circ$ C).

Evseev (17) has determined the surface tension of molten CaF_2 - Al_2O_3 fluxes at $1,600^\circ$ C by means of the maximum bubble pressure technique. This author obtained values ranging from 255 erg cm^{-2} for CaF_2 to 241 erg cm^{-2} for 60CaF_2 - $40\text{Al}_2\text{O}_3$. The slight inverse relationship between Al_2O_3 content and surface tension is attributed to the expulsion of AlOF_2^- ions into the surface layer of the flux.

CaF₂-MgO

Fluxes in the CaF₂-MgO system have been used to a limited extent in the electroslag process. Compositions have included 20 weight-percent MgO (Soviet designation ANF-9) (30) and 10 and 5 weight-percent MgO (14). Fluxes containing more than 20 weight-percent MgO make the electroslag process difficult to operate. The viscosity at 1,400° C increases from 0.23 poise for CaF₂ to 0.83 poise for 80CaF₂-20MgO (24). Slight increases in molten flux densities (from 2.55 and 2.6 g cm⁻³ for CaF₂ at 1,600° and 1,500° C, respectively, to 2.65 and 2.7 g cm⁻³ for 80CaF₂-20MgO at the same respective temperatures) have been noted (24). When MgO is added to CaF₂ fluxes, the surface tension increases from 258 to 351 erg cm⁻² at 1,500° C for 80CaF₂-20MgO, and from 253 to 346 erg cm⁻² at 1,600° C (24).

A simple eutectic characterizes the CaF₂-MgO system. Budnikov and Tresviatskii (7) give a eutectic composition of 90.1 weight-percent CaF₂ at a temperature of 1,350° C. Schlegel (50) gives the composition as 88 weight-percent CaF₂ at 1,353° C. Both sources show hypoeutectic liquidus curves concave upward extending toward the MgO composition.

Fluxes in the CaF₂-MgO system are also capable of desulfurizing metals in the electroslag process, although the capacities are lower on a molar basis compared with CaF₂-CaO fluxes, as pointed out by Davies, Hawkins, and Smith (13). Small amounts of CaO are usually present in CaF₂-MgO fluxes for reasons discussed previously in this chapter.

Other Oxides With CaF₂ and BaF₂

A number of years ago, the Soviets devised a 80CaF₂-20BaO electroslag flux (ANF-20) which was claimed to reduce phosphorus in some steels (30). Phosphorus reductions of from one-half (0.029 to 0.015 percent) to two-thirds (0.054 to 0.018 percent) were claimed (33). Williams (54) also demonstrated phosphorus reductions of one-half with a 70CaF₂-30BaO flux, although this author claimed that CaF₂-CaO fluxes removed phosphorus equally well. Disadvantages such as high cost and erratic melt operation due to the difficulty in quenching the initial arc in the electroslag process (54) have prevented BaO from becoming more than an experimental component of electroslag fluxes. At high CaF₂ contents, BaO additions depress the freezing point to a greater degree (~30° C at 80 weight-percent oxide) than

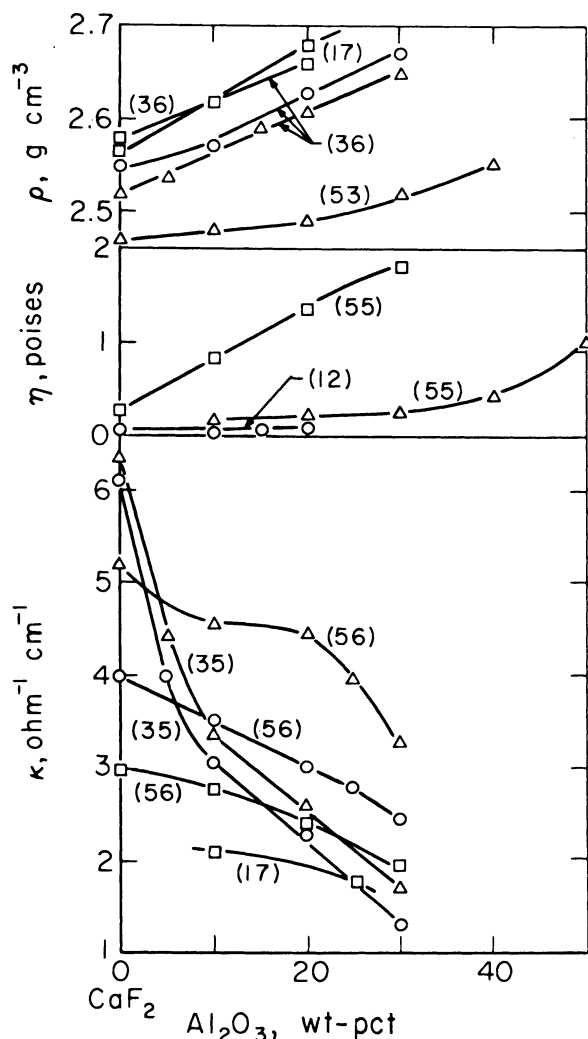


Figure 33.—Physicochemical properties of CaF₂-Al₂O₃ fluxes. κ = specific electrical conductivity, η = viscosity, ρ = density. $\square$ = 1,400° C, $\circ$ = 1,500° C, and $\triangle$ = 1,600° C. Numbers in parentheses refer to references at end of this chapter.

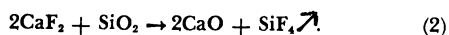
Fluxes in the CaF₂-Al₂O₃ system possess advantages such as low energy consumption, silicate inclusion removal, and nonsusceptibility to hydration. On the other hand, Al₂O₃ is relatively expensive (14), globular oxide inclusions are more easily formed in the melted metal, and faster melting rates which can reduce refining capabilities are likely to prevail.

for the case of CaO (25). The 80CaF₂-20BaO composition possesses a liquidus temperature of ~1,330° C and is probably located near the eutectic composition. A eutectic temperature of less than 1,325° C is postulated. Decreases in specific electrical conductivity from ~6.5 ohm⁻¹cm⁻¹ for CaF₂ to ~5.8 ohm⁻¹cm⁻¹ for 80CaF₂-20BaO at 1,600° C have been observed (17). These decreases are comparable to those noted for CaO additions. Similar decreases in viscosities have also been qualitatively noted (30).

Among group IV oxides, SiO₂, ZrO₂, and TiO₂ have been added to CaF₂ in order to form two-component experimental electroslag fluxes which might modify the chemistry of electroslag-melted metal.

The pseudobinary system CaF₂-SiO₂ is characterized by a eutectic at 98 weight-percent CaF₂ and 1,370° C (19). A large liquid immiscibility region (>1,500° C) extends from the eutectic to the SiO₂ composition. This is bounded at ~1,400° C by a three-phase region composed of two liquids and tridymite (19). Latash and Medovar (30) have demonstrated that the surface tension decreases from ~400 erg cm⁻² for pure CaF₂ to 340 erg cm⁻² for a 66CaF₂-34SiO₂ composition at 1,400° to 1,560° C. Decreases in specific electrical conductivity from ~6.1 ohm⁻¹cm⁻¹ for CaF₂ to ~5.5 ohm⁻¹cm⁻¹ for 85CaF₂-15SiO₂ at 1,500° C have been noted (28). Such decreases are considerably less than those noted for equivalent Al₂O₃ additions (fig. 33). Silica additions to CaF₂ decrease molten flux densities (51).

Williams (54) has used a 90CaF₂-10SiO₂ flux to electroslag-melt En 42 steel (chapter 12). This author observed an approximately 25-percent decrease in sulfur, oxygen, and manganese from electrode to ingot. Other elements were unaffected. Soviet investigators have used ≥92CaF₂-≤5SiO₂ (ANF-1) fluxes to electroslag-melt some high-alloy steels. Silica additions, however, are not regarded as suitable for electroslag fluxes because of relatively low thermodynamic stability, increased flux-metal adhesion, reduced desulfurization potential, and the presence of the troublesome reaction (30)



Titanium dioxide (TiO₂) is sometimes added to electroslag fluxes to obtain greater conductivity in the solid state for easier cold starts, and to inhibit titanium removal from the electrode metal. According to Hillert (19), the CaF₂-TiO₂

system is a simple eutectic type with the eutectic at 1,365° C and 70 weight-percent CaF₂. Slightly lower specific electrical conductivity values and comparable surface tension values of molten CaF₂-TiO₂ fluxes compared with CaF₂-SiO₂ fluxes were noted at 1,500° C (17, 30). Additions of TiO₂ to CaF₂ fluxes increase the densities (51).

Soviet investigators have also developed a 80CaF₂-20ZrO₂ flux (ANF-19) which was claimed to possess the capability of high heat liberation, acid properties with greater thermodynamic stability than silica, and relatively low viscosity (30). Nearly identical surface tension values and lower specific electrical conductivity values were observed, compared with those of CaF₂-TiO₂ fluxes at 1,500° C (17, 30). Densities are increased when ZrO₂ is added to CaF₂ fluxes (51). Fluxes in the CaF₂-ZrO₂ system, however, are relatively expensive.

Oden, Sanker, Babitzke, and Sumner (41-42) have studied phase equilibrium relations in the systems CaF₂-Y₂O₃ and BaF₂-Y₂O₃ for possible use as fluxes in the electroslag process. The CaF₂-Y₂O₃ pseudobinary system shows a peritectic composition of 82 weight-percent CaF₂ at 1,438° C. The solid solubility of Y₂O₃ in CaF₂ ranges from 18 weight-percent at 1,438° C to 3 weight-percent at 1,100° C, and the solubility of CaF₂ in Y₂O₃ decreases from 3.5 to 2.5 weight-percent at the same temperatures. The liquidus increases from 1,438° C at ~0.7 weight-percent CaF₂ to ~2,000° C at 34 weight-percent CaF₂, and its shape suggests strong positive deviation from ideality for the liquid. Suitable electroslag fluxes are thus confined to compositions greater than ~93 weight-percent CaF₂.

The BaF₂-Y₂O₃ system is a simple eutectic system with the eutectic composition less than 1.2 weight-percent Y₂O₃ at 1,343° C. Maximum terminal solid solubilities are less than 1.2 weight-percent. Liquidus temperatures increase rapidly to ~2,000° C at 20 weight-percent Y₂O₃; the shape of the liquidus curve is similar to that of CaF₂-Y₂O₃.

Period 4 transition metal oxides are not normally deliberately added to electroslag fluxes. Because of their variable valency, they can act as a convenient medium for oxygen transfer, often detrimentally increasing the oxygen potential in the slag. This, in turn, inhibits maximum metal deoxidation and increases oxidative losses of alloying elements. Transition metal oxides usually occur as flux impurities in used material. These impurities can be minimized by

more expensive melting in inert atmospheres. Williams (54) has added up to 40 weight-percent Fe_2O_3 to CaF_2 fluxes in an effort to remove phosphorus during electroslag melting under oxidizing conditions. Phosphorus typically decreased threefold (from 0.034 to 0.013 percent) with this flux. Decreases of silicon and manganese were also noted.

TERNARY OXYFLUORIDE SYSTEMS

$\text{CaF}_2\text{--CaO--Al}_2\text{O}_3$

One of the most important systems that have found wide application in the electroslag process is $\text{CaF}_2\text{--CaO--Al}_2\text{O}_3$. Despite the extensive use of compositions in this system for electroslag fluxes, very little has appeared in the literature with respect to the delineation of liquidus temperatures, solidus-liquidus temperature ranges, and primary phases in an environment directly applicable to the electroslag process. All of the aforementioned parameters are important for intelligently selecting optimum electroslag fluxes.

The three boundary joins have been the subject of considerable work, however. The binary joins $\text{CaF}_2\text{--CaO}$ and $\text{CaF}_2\text{--Al}_2\text{O}_3$ have been discussed earlier in this chapter. It is generally agreed that the system $\text{CaO--Al}_2\text{O}_3$ contains four incongruently-melting compounds ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$, $\text{CaO}\cdot\text{Al}_2\text{O}_3$, $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$, $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$) (21, 40). An additional compound ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$), which melts congruently, is present under conditions applicable to electroslag remelting. In rigorously dry atmospheres, however, this compound is believed to be unstable (40).

Various workers have studied portions of the $\text{CaF}_2\text{--CaO--Al}_2\text{O}_3$ system, beginning with Eitel (16) in 1938, who delineated a ternary eutectic. Subsequently, authors found liquidus minima corresponding to postulated invariant points (55), areas of liquid immiscibility in sealed samples (8-9, 18-19), at least two ternary compounds (8-9, 18, 31, 57), nine subsolidus fields (8), and a small stability field of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ adjacent to the $\text{CaO--Al}_2\text{O}_3$ join (11). Costa and Massazza (11) also have determined the heats of formation of the cubic $11\text{CaO}\cdot 7\text{Al}_2\text{O}_3\cdot\text{CaF}_2\text{--}12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ phase. Zhmoidin and Chatterdzhi (57) have shown that the liquidus temperatures in the $\text{CaF}_2\text{--Al}_2\text{O}_3$ join differ imperceptibly, whereas those in the $\text{CaO--}70\text{CaF}_2\cdot 30\text{Al}_2\text{O}_3$ join vary $\leq 85^\circ\text{C}$ between open (argon atmosphere) and closed (sealed capsules) conditions. These authors noted, however, that phase assemblages and crystallization sequences varied as a function of

the experimental method. These differences were attributed to the volatilization of AlF_3 formed from a reaction of CaF_2 with Al_2O_3 , and/or the formation of HF derived from the reaction of CaF_2 and H_2O in an open atmosphere. To the author's knowledge, however, no systematic study of the entire system of liquidus temperatures under conditions that are directly applicable to the electroslag and other metallurgical processes has been reported.

The purpose of the work reported herein is, therefore, to simultaneously determine all of the parameters in the important flux system $\text{CaF}_2\text{--CaO--Al}_2\text{O}_3$ mentioned earlier in this chapter in an environment of $1/3$ atm helium which is used in the electroslag remelting processes as practiced in our laboratory.

Experimental Work

Reagent-grade powders were used as the starting materials. The CaF_2 was fused in a molybdenum-alloy liner (0.22 weight-percent carbon, 0.05 weight-percent titanium, 0.08 weight-percent zirconium) contained in a graphite resistor furnace under $1/3$ atm of backfilled helium. The CaO and Al_2O_3 powders were heated at 800°C for 4 to 8 hours in air and contained 0.2 to 0.7 weight-percent impurities after heating. X-ray and optical determinations showed only the presence of the pure oxides. Forty-gram mixtures were weighed in the correct proportions, ground, mixed to ensure homogeneity, and stored in desiccators.

Since CaF_2 - and CaO -rich compositions cannot be quenched, all mixtures were subjected to thermal analysis and DTA determinations as described in chapter 5, except that the mixtures were contained in molybdenum-alloy crucibles of the aforementioned composition to preclude graphite contamination. No interaction of the sample with the crucible, thermocouple sheath and insulation, or furnace atmosphere was observed. The composition of each mixture after heating and cooling as determined by wet chemistry techniques, varied less than 1 weight-percent from the nominal composition of the starting mixture. Several replicate runs on each mixture served to delineate the variance of the temperature determinations. Liquidus and solidus temperatures were determined by visual observation, from the heating and cooling curves, and from the DTA peaks for each mixture. After the runs, the phases were identified by optical microscopy and X-ray powder diffraction methods.

Attainment of the expected quickly reached equilibrium was checked by subjecting selected mixtures to temperatures above and below the estimated liquidus for varying lengths of time. Comparisons of the runs for each mixture demonstrated a consistent phase assemblage by X-ray and optical techniques in all samples. Replicate thermal analysis determinations invariably yielded identical phase assemblages for a given composition. Optically determined crystal texture and morphology also indicated that equilibrium

conditions with constant crystallization sequences prevailed. In addition, no significant differences were noted between results obtained from the heating and cooling curves.

Results

The liquidus diagram of the system CaF_2 - CaO - Al_2O_3 under $\frac{1}{3}$ atm helium as determined by the aforementioned techniques is presented in figure 34. Data for the limiting binary systems were taken from the literature (6, 21, 34). Six

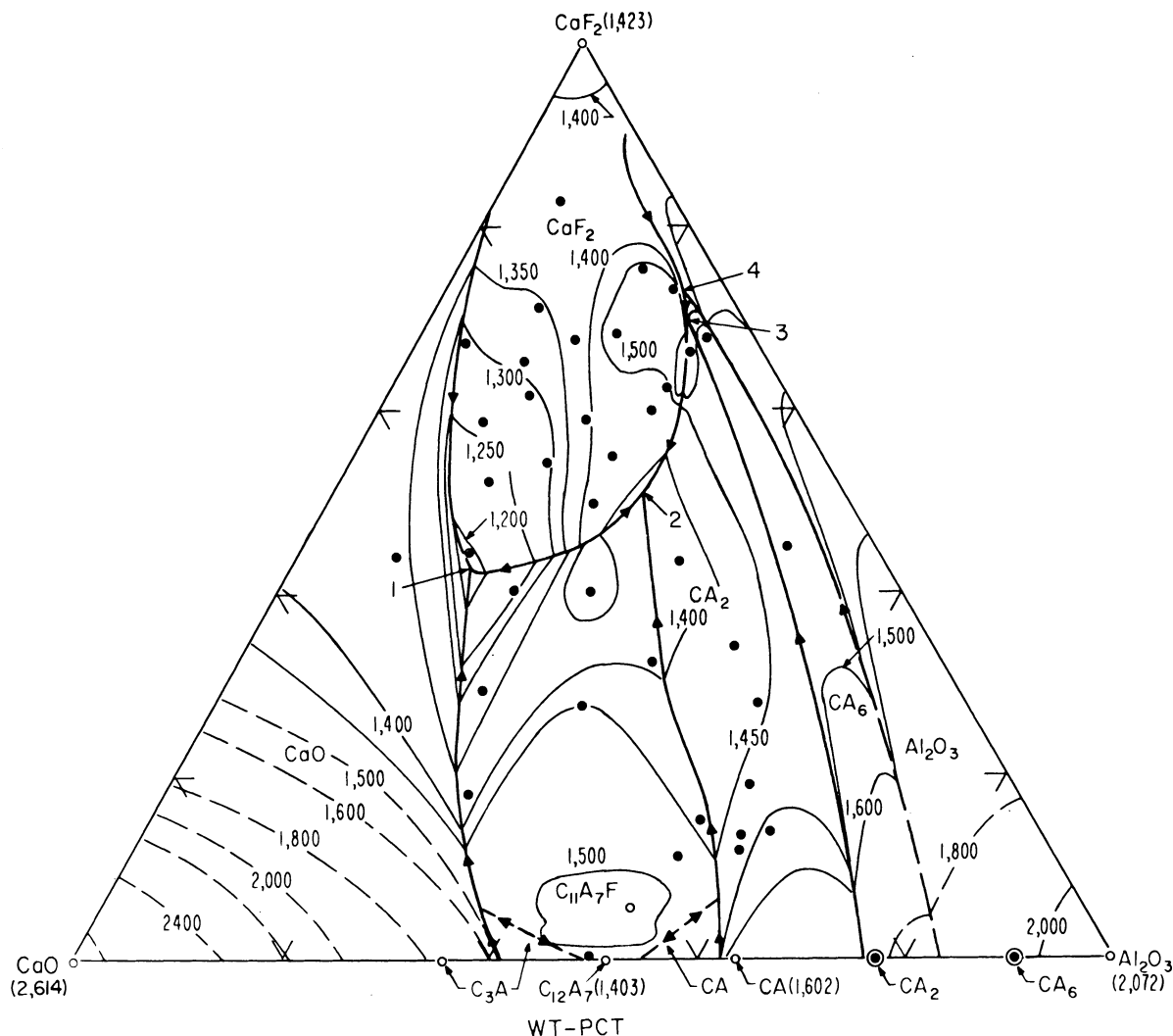


Figure 34.— Liquidus diagram of the system CaF_2 - CaO - Al_2O_3 under $\frac{1}{3}$ atm helium showing phase boundaries and liquidus isotherms, both of which are dashed where inferred. Open circles represent compounds, filled circles denote compositions of mixtures after thermal analysis, temperatures are indicated in degrees Celsius, and arrows on the boundary curves show direction of decreasing temperature. Abbreviations for phases are: $\text{C}_3\text{A} = 3\text{CaO} \cdot \text{Al}_2\text{O}_3$; $\text{CA} = \text{CaO} \cdot \text{Al}_2\text{O}_3$; $\text{C}_{11}\text{A}_7\text{F} = 11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ solid solution; $\text{C}_{12}\text{A}_7 = 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$; $\text{CA}_2 = \text{CaO} \cdot 2\text{Al}_2\text{O}_3$; $\text{CA}_6 = \text{CaO} \cdot 6\text{Al}_2\text{O}_3$.

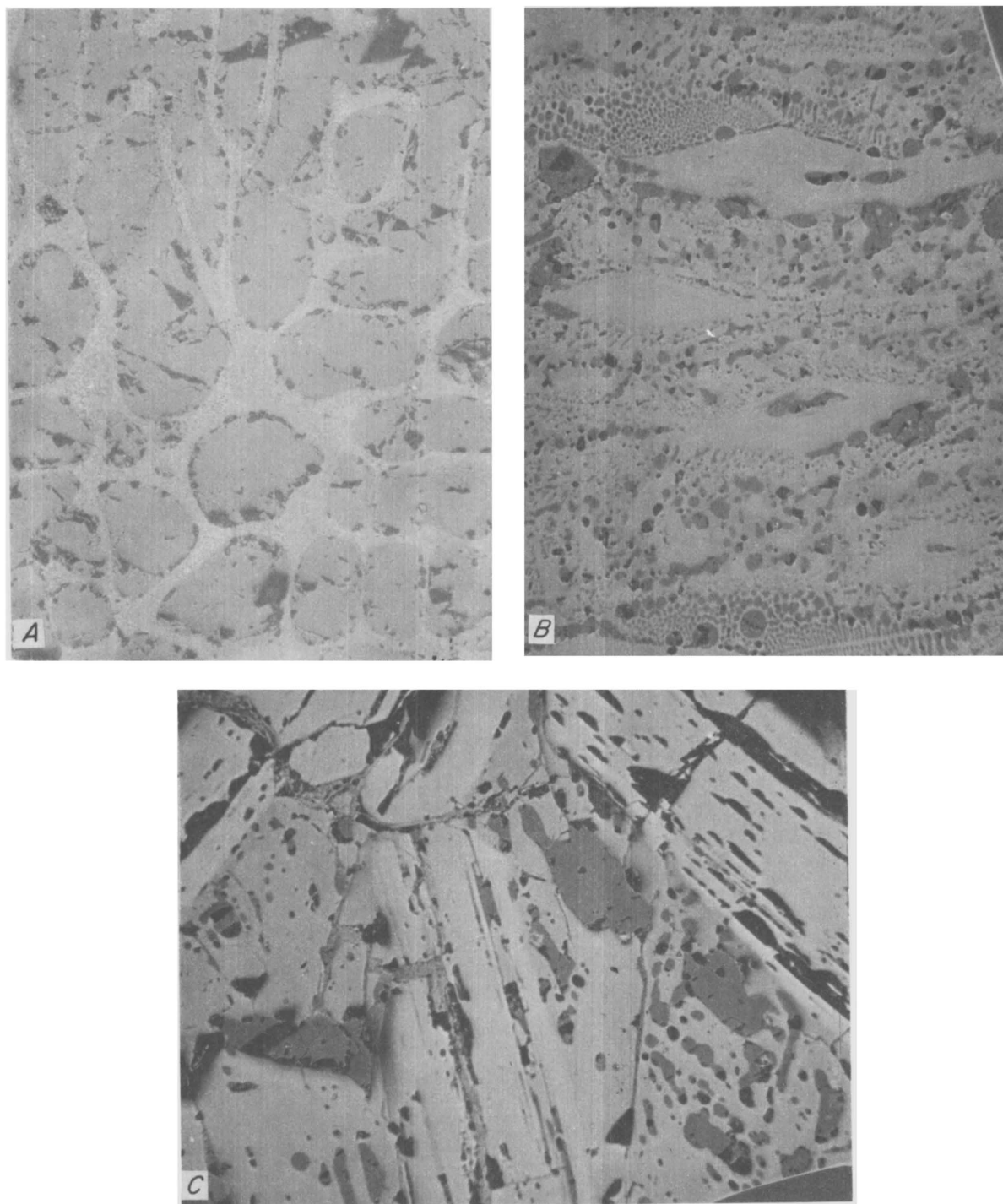


Figure 35.—Solid phase assemblages at the three determined eutectics in the system CaF_2 - CaO - Al_2O_3 . *A*, Primary dark grains of CaF_2 in a eutectic matrix of $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ solid solution and CaO (light); mixture composition is (weight-percent) 83.2CaF_2 - 10.7CaO - $6.1\text{Al}_2\text{O}_3$. *B*, Primary euhedral grains of $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ in a eutectic matrix of $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ solid solution and CaF_2 ; mixture composition is (weight-percent) 30.2CaF_2 - 27.3CaO - $42.5\text{Al}_2\text{O}_3$. *C*, Primary laths of $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ (lightest phase) in a matrix of $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ (medium) and CaF_2 (dark); mixture composition is (weight-percent) 45.0CaF_2 - 8.7CaO - $46.3\text{Al}_2\text{O}_3$.

invariant points are shown. Three eutectics and one peritectic were confirmed in the present work. Two additional peritectics at low CaF_2 contents were postulated as shown, in accordance with phase diagram theory and published results of the $\text{CaO}-\text{Al}_2\text{O}_3$ system (21). Pertinent data for the determined invariant points are shown in

table 11. Solid phase assemblages at the three experimentally determined eutectics are shown in the photomicrograph of figure 35. These represent the phases present upon crystallization after thermal analysis treatment of three different compositions, each lying within a different compatibility triangle (fig. 36).

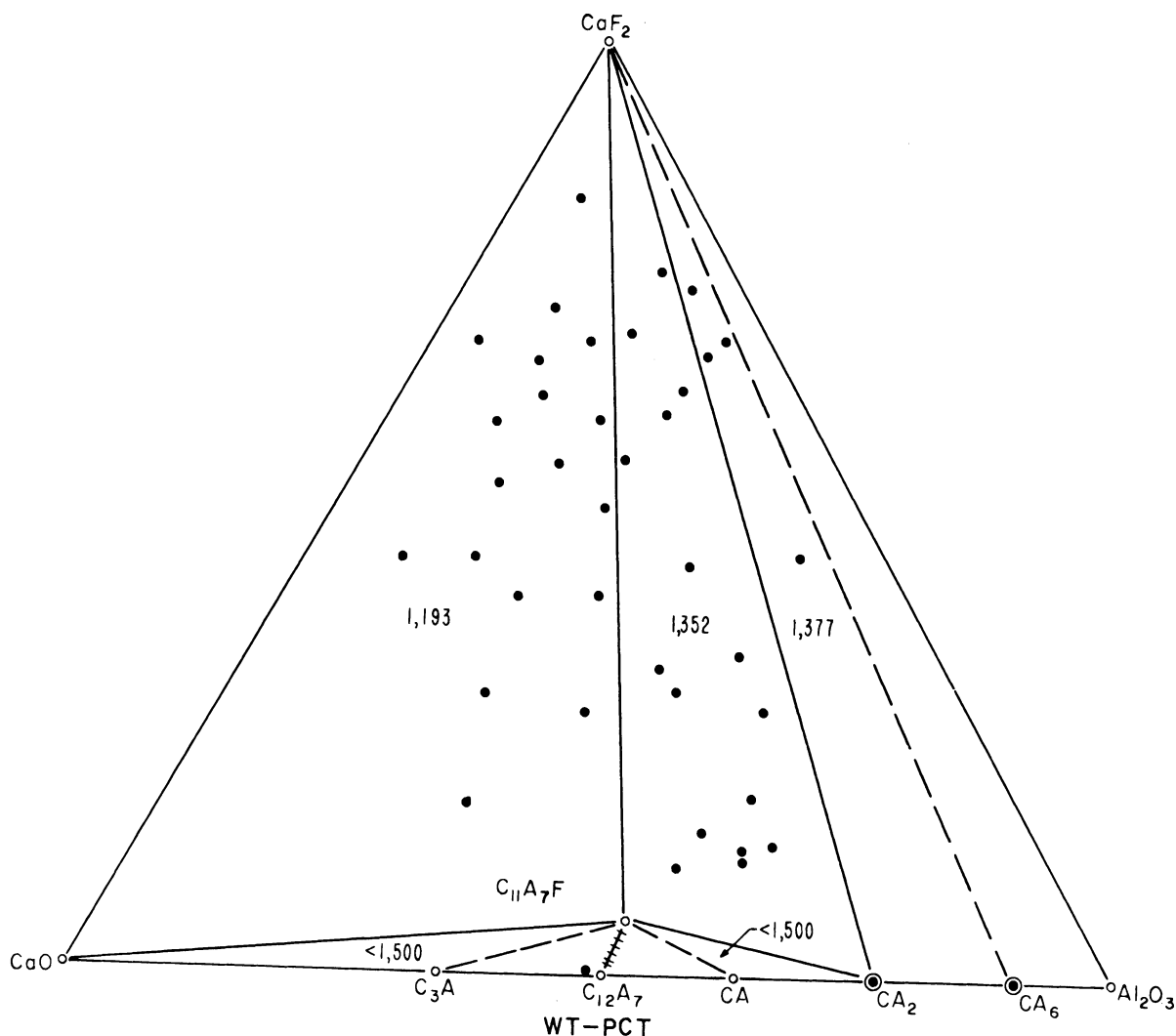


Figure 36.—Solidus diagram of the system CaF_2 - CaO - Al_2O_3 under $\frac{1}{3}$ atm of helium. Temperatures in degrees Celsius are solidus temperatures for all compositions lying within each compatibility triangle outlined by solid lines. Abbreviations for phases are $\text{C}_3\text{A} = 3\text{CaO} \cdot \text{Al}_2\text{O}_3$; $\text{CA} = \text{CaO} \cdot \text{Al}_2\text{O}_3$; $\text{C}_{11}\text{A}_7\text{F} = 11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ solid solution; $\text{C}_{12}\text{A}_7 = 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$; $\text{CA}_2 = \text{CaO} \cdot 2\text{Al}_2\text{O}_3$; $\text{CA}_6 = \text{CaO} \cdot 6\text{Al}_2\text{O}_3$. Dashed lines define one boundary of three phase triangles whose components are the solid phases present at the peritectic points (see figure 34). The cross-hatched line indicates solid solution between C_{12}A_7 and $\text{C}_{11}\text{A}_7\text{F}$. Therefore the lines emanating from CaO , C_3A , CA , and CA_2 , and extending to $\text{C}_{11}\text{A}_7\text{F}$, can terminate anywhere along the C_{12}A_7 - $\text{C}_{11}\text{A}_7\text{F}$ join, depending on the composition of the solid solution in equilibrium with the other phases at solidus temperatures.

Table 11.—*Determined invariant points in the system CaF_2 - CaO - Al_2O_3*

Designation (fig. 34)	Composition, wt-pct			Temperature, °C	Solid phase assemblage ¹	Type
	CaF_2	CaO	Al_2O_3			
1	43	40	17	$1,193 \pm 5$	CaF_2 - CaO - $\text{C}_{11}\text{A}_7\text{F}$	Eutectic.
2	51	19	30	$1,352 \pm 7$	CaF_2 - CA_2 - $\text{C}_{11}\text{A}_7\text{F}$	Do.
3	69	6	25	$1,377 \pm 4$	CaF_2 - CA_2 - CA_6	Do.
4	73	4	23	1,389	CaF_2 - CA_6 - Al_2O_3	Peritectic.

¹ Meanings of abbreviations are given in figure 34 legend.

Solidus temperatures for compositions in the CaF_2 - CaO - Al_2O_3 system under $1/3$ atm helium are shown in figure 36. This diagram also gives the compatibility triangles as derived from figure 34. Hence, by consulting both figures 34 and 36, the melting range of any flux composition within this system can be ascertained.

The hexagonal phase $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$, with a large c-axis, is readily identified optically as radiating laths and fibers and/or as hexagonal forms with a greater reflectivity than other hexagonal phases encountered in this system. However, the phase was difficult to identify by X-ray powder diffraction methods. This is believed due to the preferred crystal orientation.

As noted in figure 34, there is an extensive primary phase field of the ternary compound $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$. This phase was identified on the basis of X-ray lattice parameter measurements on ternary samples subjected to thermal analysis. The cubic lattice parameter averaged $11.9118 \text{ \AA} \pm 0.006$, whereas for $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ synthesized from the oxides alone, the lattice parameter was $11.9436 \text{ \AA} \pm 0.005$. The observed contraction of the unit cell is expected when the structure substitutes fluorine for oxygen anions according to the reaction



Details concerning this transformation have been given previously (4). Costa and Massazza (11) have determined that complete solid solubility exists between $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ and $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$. A singular point at $(12-x)\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot x \text{CaF}_2$ ($x=0.8$) may exist in this solid solution, based on experiments with SiO_2 (32).

Discussion

Although as mentioned earlier, phase equilibrium determinations in the system CaF_2 - CaO - Al_2O_3 conducted in sealed capsules are of limited practical use to actual technological processes, it is of interest to compare and contrast these determinations with those of the present study.

There are two major differences between the liquidus diagram of the present work constructed from results of runs conducted under $1/3$ atm of helium (fig. 35) and that presented by Chatterdzhii and Zhmoidin (9) for sealed-capsule runs. Experimental results in a closed system demonstrate the presence of an extensive region of two immiscible liquids, extending from approximately 35 to 98 weight-percent CaF_2 in the Al_2O_3 -rich portion of the ternary diagram. This region was detected by other workers in sealed-capsule assemblages, as mentioned previously (18-19). In contrast to this, no liquid immiscibility was detected in the run products of any of the mixtures in the present study. Experiments under $1/3$ atm helium with a hot-filament cell, in which the sample could be observed with a binocular microscope during the heating and cooling, also failed to show two liquids at either high or low temperatures. It is believed that under the conditions of the present determinations, small amounts of fluoride volatilize³; this precludes two-liquid formation, since one of the liquids must be fluoride-rich. Relatively low bulk fluoride contents in the present mixtures further reduce the possibility of two-liquid formation. Mitchell and Burel (34) also failed to detect a liquid miscibility gap in the CaF_2 - Al_2O_3 join in an argon atmosphere. Electrical conductivity measurements in a nitrogen atmosphere by Bääk (1) revealed a small two-liquid region in the CaF_2 - CaO system (fig. 31). However, it is possible that poor quenching techniques or contamination caused this, since Mukerji (37) reports no liquid immiscibility formation in sealed-capsule experiments in this system. A liquid miscibility gap was also reported as a result of quenching by Mitchell and Cameron (35) for the CaF_2 - CaO - Al_2O_3 system in an argon atmosphere during electrical conductivity measurements.

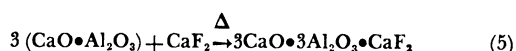
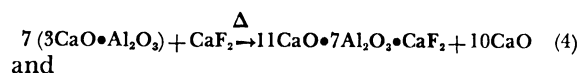
The second major difference attributable to the ambient atmosphere was the absence of the

³ Not enough, however, to appreciably change the bulk composition of the mixtures, as observed previously.

ternary compound $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ in the present work. Although minor amounts of this phase were detected in a few of the present runs, its presence is considered to be metastable and not compatible with the $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ phase in $1/3$ atm helium. This conclusion was presented by Chatterdzhi, Malysheva, and Zhmoidin (8) for an argon atmosphere.

Aside from the aforementioned factors, a smaller CaF_2 primary phase field, and the absence of Al_2O_3 coexisting with CaF_2 , the liquidus diagram of mixtures heated in sealed capsules is similar to figure 34.

The small postulated stability fields of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (fig. 34) in the CaF_2 - CaO - Al_2O_3 system can be attributed to the high-temperature reaction of these compounds with CaF_2 as follows:



These reactions have been postulated by Brisi and Rolando (4-5). The formed ternary compound decomposes at high temperatures in an "open" system to form probably $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ and $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ (8). Masazza and Pezzuoli (32) also observed a reduction of the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ phase field with CaF_2 additions to CaO , Al_2O_3 , and SiO_2 . However, compositions in this region are not normally used as fluxes in the electroslag process because of the relatively high electrical resistivity and viscosities encountered.

If the phase boundary curves of figure 34 are removed, the liquidus surface exhibits characteristics similar to those presented by Zhmoidin on the basis of viscosity data (55). Figure 34 shows primary phase fields as a function of composition. Thus, it is possible to closely estimate the temperature at which the first solid phase begins to crystallize for any given flux composition. This information plays an important role in ingot surface quality during electroslag melting (15). Typical liquidus temperatures for specialty steels and superalloys range from $1,270^\circ$ to $1,480^\circ$ C. Therefore, it can be seen from figure 34 that a wide variety of these materials can be remelted by the electroslag process using fluxes in this system, since, in general, it is desirable to maintain the flux liquidus temperature slightly below that of the metal to be melted.

The liquidus diagram of the system CaF_2 - CaO - Al_2O_3 depicted in figure 34 probably repre-

sents very closely the relations in an air atmosphere. Some hydrolysis of CaF_2 , forming CaO , would undoubtedly occur, causing an increase in the CaO stability area at the expense of the CaF_2 field. Hydrolysis of CaO , however, would probably further modify this primary phase field. The boundary system CaO - Al_2O_3 is not likely to be binary in air due to the hydrolysis of $12\text{CaO} \cdot \text{Al}_2\text{O}_3$, causing a $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ phase to form. However, this phase would probably not extend very far into the system CaF_2 - CaO - Al_2O_3 , either because of the competition for vacant lattice sites in the cubic $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ structure by CaF_2 , or because of thermal hydrolysis between CaF_2 and H_2O .

Physicochemical Properties

One of the most important physical properties of electroslag fluxes is the specific electrical conductivity. This parameter largely determines heat distribution and generation during electroslag melting. Mitchell and Cameron (35) have discussed reasons for discrepancies in measurements reported in the literatures. These include (1) unknown liquid composition due to hydrolysis, fluoride volatilization, and/or sample-crucible reactions, (2) ill-defined cell constants as a function of cell geometry, and (3) unknown dependence of cell reactions on the frequency of the measurements. Mitchell and Cameron's results (35) have been replotted in terms of the ternary diagram and are shown at two temperatures of interest in figures 37 and 38. These authors defined their cell geometry and frequency (1kHz), determined the optimum electrode immersion depth for a negligible effect on the cell constant, and conducted their runs in molybdenum crucibles. Superimposed on their results in figures 37 and 38 are those of Zhmoidin (56). This author considered similar cell parameters but used a different cell design. Zhmoidin's (56) values are higher than those given by Mitchell and Cameron (35). These differences may be attributed to a capacitance effect in Zhmoidin's cell and/or to CaF_2 hydrolysis. Figures 37 and 38 reflect the greater effect of Al_2O_3 compared with CaO in reducing electrical conductivity on a weight-percent basis. Also noteworthy is the area of relatively low conductivity values located near the $\text{CaO}:\text{Al}_2\text{O}_3 = 1:1$ weight ratio join. Zhmoidin (56) has attributed this to the change of the coordination number of aluminum from 6 to 4 and subsequent silica-type polymerization near the 1:1 ratio. Fluxes in this area

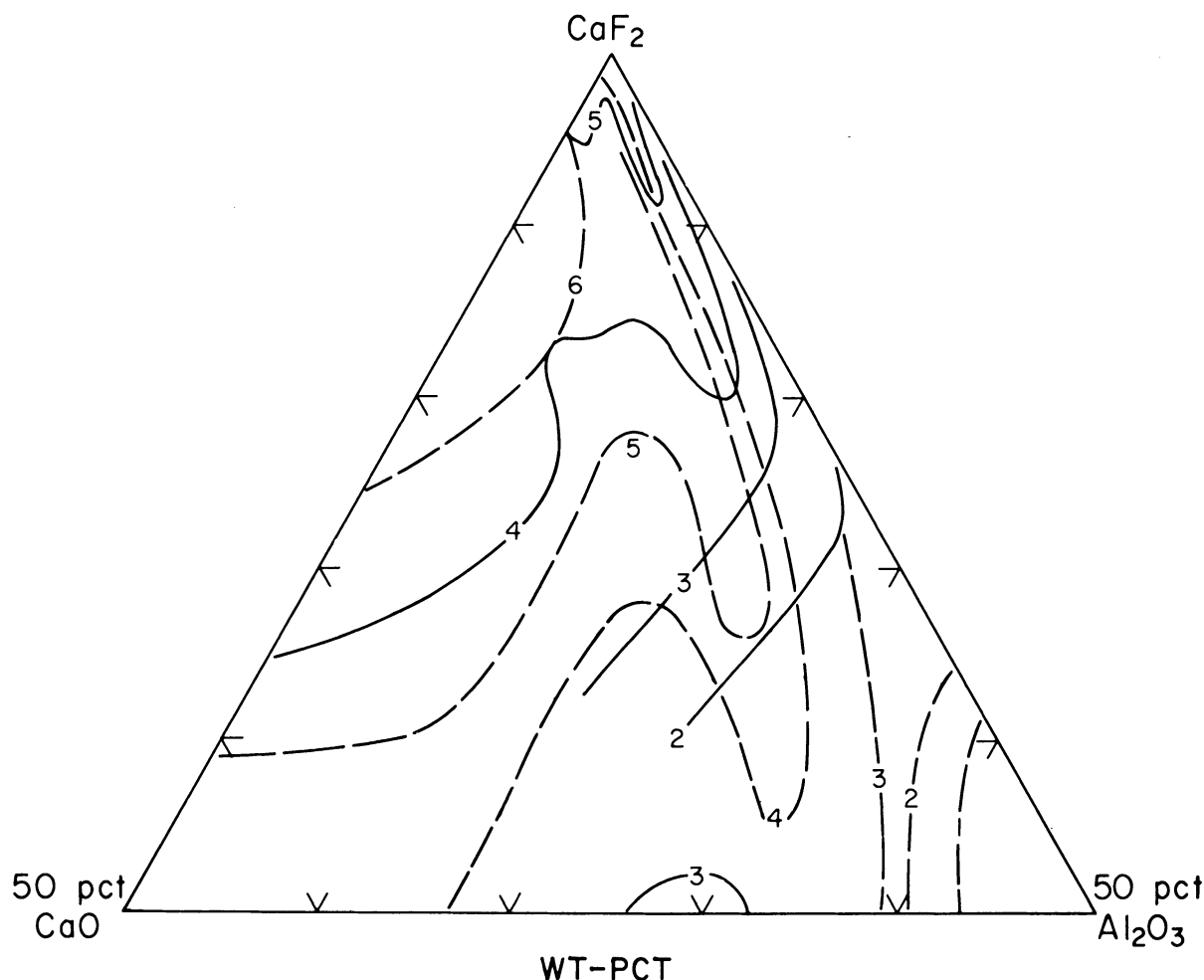


Figure 37.—Specific electrical conductivity ($\text{ohm}^{-1} \text{cm}^{-1}$) in the CaF_2 -rich portion of the system CaF_2 - CaO - Al_2O_3 at $1,500^\circ \text{C}$. Solid curves were derived from Mitchell and Cameron (35), and dashed curves are from Zhmoidin (56).

can, therefore, contain more CaF_2 (for example, for viscosity considerations) and yet remain sufficiently resistive to support required current densities without undesirable arcing during electrosag melting. This partially accounts for the popularity of such fluxes as 70CaF_2 - 15CaO - $15\text{Al}_2\text{O}_3$, 60CaF_2 - 20CaO - $20\text{Al}_2\text{O}_3$, and 40CaF_2 - 30CaO - $30\text{Al}_2\text{O}_3$. Small amounts of CaO increase the conductivity of CaF_2 - Al_2O_3 melts due to the replacement of $\text{AlO}_2\text{F}_2^{3-}$ and AlOF_2^- by AlO_3^{3-} and AlO_2^- (35). This releases more fluoride ions with greater mobility into the melt.

Flux viscosity not only determines the velocity of molten metal drops falling through the flux during electrosag melting, but also influences the kinetics of certain metal-flux reactions. Re-

sults of high-temperature viscosity determinations in the CaF_2 - CaO - Al_2O_3 system using the rotating crucible method (12) and a vibrating electrical viscosimeter (45) are summarized in figure 39. Zhmoidin (55) has also presented viscosity data for this system showing higher values than those presented in figure 39. This could be explained by the presence of CaO as a result of CaF_2 hydrolysis, or other complexing impurities. With greater oxide contents, flux viscosities increase, probably because of the formation of less mobile alumina-oxyfluoride anions of the type discussed earlier in this chapter. Areas of relatively low viscosity are again centered near the $\text{CaO}:\text{Al}_2\text{O}_3 = 1:1$ join as can be seen from figure 39. Lower flux viscosities reduce nonmetallic inclu-

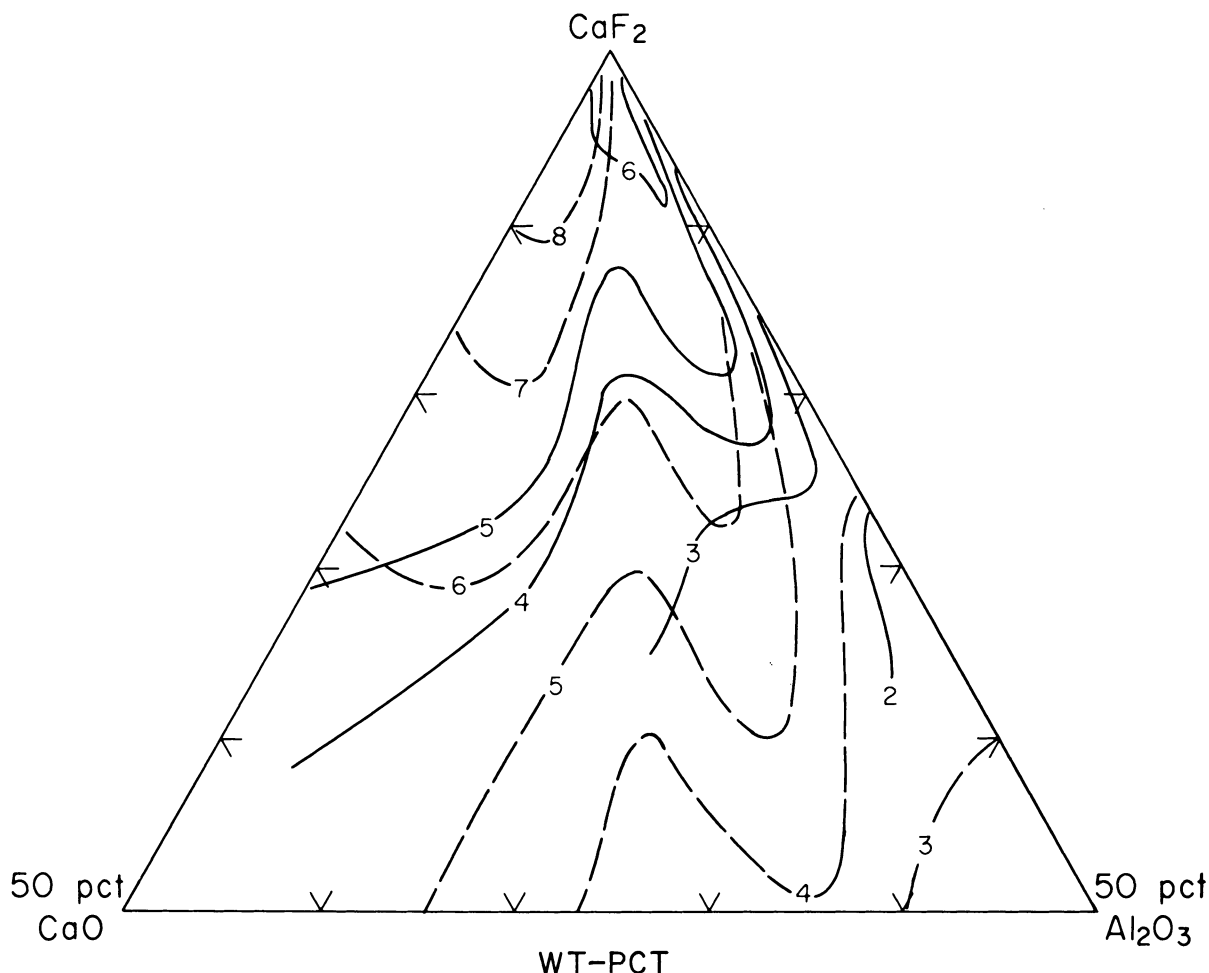


Figure 38.—Specific electrical conductivity ($\text{ohm}^{-1} \text{ cm}^{-1}$) in the CaF_2 -rich portion of the system $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3$ at $1,600^\circ \text{ C}$. Solid curves were derived from Mitchell and Cameron (35), and dashed curves are from Zhmoidin (56).

sions in electroslag-melted ingots and are believed to enhance flux refining properties. These factors further indicate the desirability of using electroslag fluxes with a 1:1 oxide weight ratio in the $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3$ system.

The density of electroslag fluxes is important insofar as it remains lower than the molten metal to prevent flux entrapment and promote metal-flux separation. Representative $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3$ flux densities are given in figure 40 (17, 53). Greater increases are noted for Al_2O_3 additions than for equivalent CaO additions to CaF_2 . This is probably again related to the aforementioned complex anion formation, ternary compound stability, and/or cation-oxygen

binding energies greater than those for cation-fluorides.

Figure 41 presents available data concerning the surface tension of fluxes in the system $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3$ as determined by bubble pressure methods in molybdenum capsules (17, 45). A greater increase in surface tension is noted for CaO additions to CaF_2 than for Al_2O_3 additions. Lime dissociates into calcium and oxygen ions, the latter of which replace fluoride anions on the surface layer, thereby increasing the binding energy of this layer with those beneath (17).

$\text{CaF}_2\text{-MgO-Al}_2\text{O}_3$

Flux compositions in the system $\text{CaF}_2\text{-MgO-Al}_2\text{O}_3$ can be used to electroslag-melt ferrous

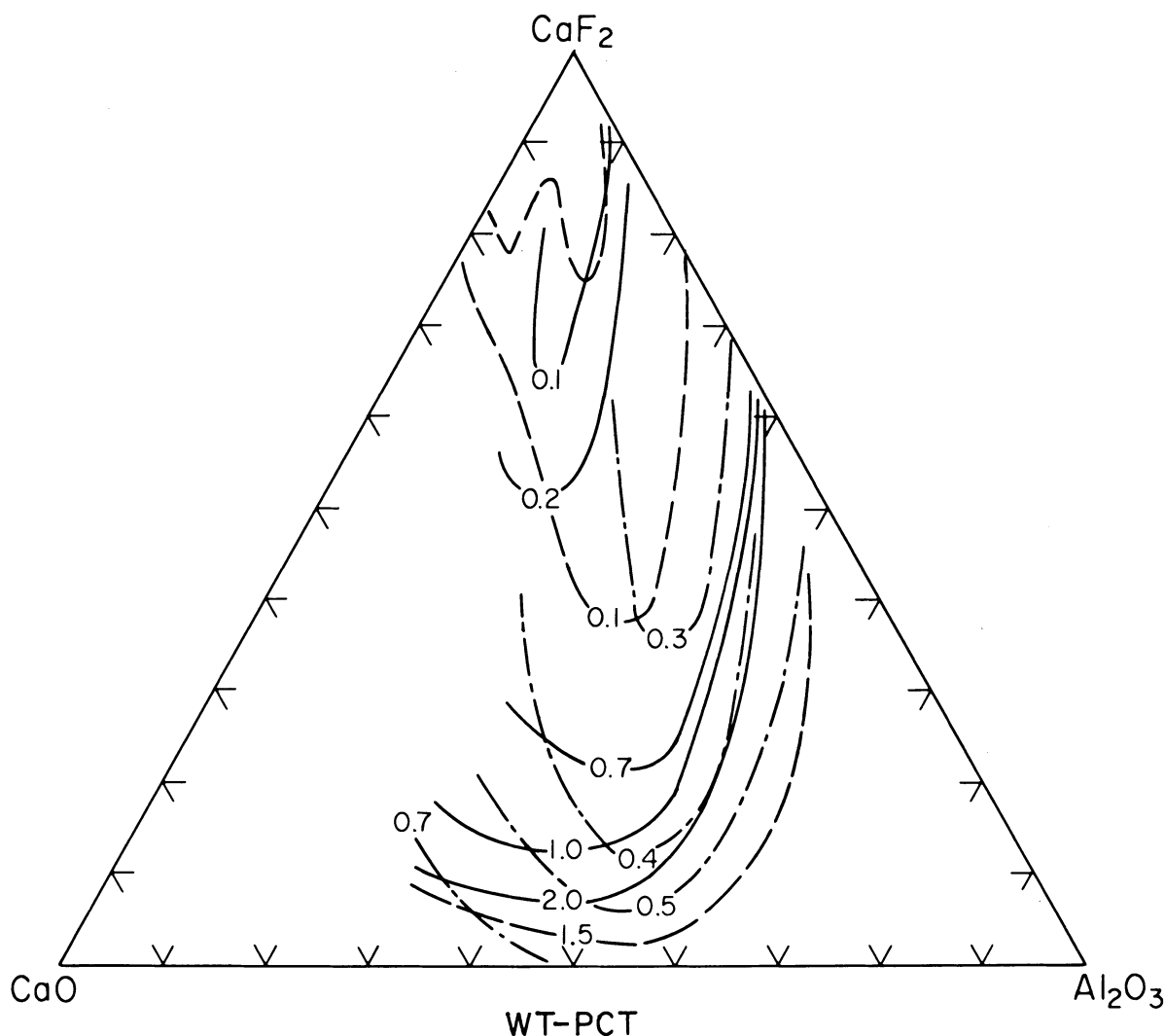


Figure 39.—Viscosity (in poise = 10^{-1} Ns/m²) of fluxes in the system CaF_2 - CaO - Al_2O_3 at 1,400° C (solid curves; 12, 45), 1,500° C (dashed curves; 12, 45), and 1,600° C (dot-dash curves, 45).

alloys containing easily oxidizable elements such as aluminum and titanium. However, appropriate compositions should contain less than 50 weight-percent Al_2O_3 and 20 weight-percent MgO , and more than 50 weight-percent CaF_2 for process stability (14). Typical compositions developed by ESRT (see chapter 1) include 60–85 CaF_2 –5–10 MgO –10–30 Al_2O_3 (weight-percent). In 1954, Holmes (20) patented a series of flux compositions in this system with compositions ranging from 25 to 55 weight-percent CaF_2 , 10 to 20 weight-percent MgO , and 35 to 65 weight-percent Al_2O_3 . These compositions, however, possess liquidus temperatures (1,450°–1,800° C) which are generally too high for practical elec-

troslag melting (14). Duckworth and Hoyle (14) have proposed a phase diagram for this system which shows two ternary eutectics at estimated compositions (weight-percent) of 84 CaF_2 –7 MgO –9 Al_2O_3 (1,280° C) and 73 CaF_2 –1 MgO –26 Al_2O_3 (1,250° C). Raichenko and Litvinova (46) reported a tenary compound of unspecified composition with 14 weight-percent MgO additions to 70 CaF_2 –30 Al_2O_3 fluxes.

CaF_2 - CaO - MgO

Salt (48) has stated that fluxes in the CaF_2 - CaO - MgO system have been used for the removal of alumina and spinel inclusions in the electroslag process. However, Bhat (2) attempted

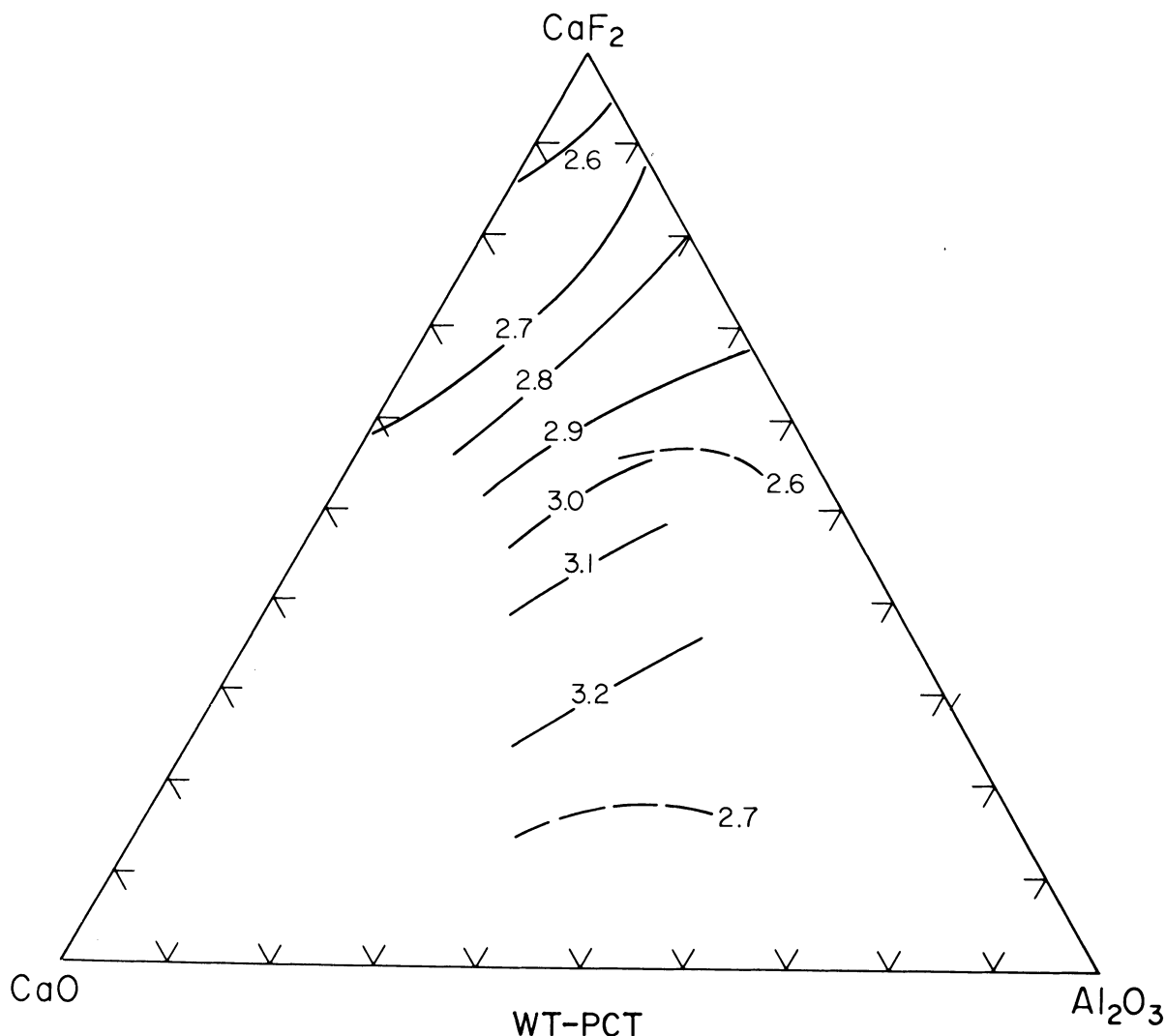


Figure 40.—Densities (g cm^{-3}) of molten fluxes in the system $\text{CaF}_2\text{--CaO--Al}_2\text{O}_3$ at $1,450^\circ\text{C}$ (solid curves, 53) and at $1,600^\circ\text{C}$ (dashed curves, 17).

without success to electroslag-remelt 18-percent nickel maraging steel using a flux composition of $80\text{CaF}_2\text{--}11\text{CaO--}9\text{MgO}$. The phase diagram as determined by Schlegel (50) contains one ternary eutectic at $71\text{CaF}_2\text{--}19\text{CaO--}10\text{MgO}$ (weight-percent) with a liquidus temperature of $1,343^\circ\text{C} \pm 4^\circ$. No stable compounds were detected.

$\text{CaF}_2\text{--CaO--SiO}_2$

Although Soviet investigators have reported using silicate fluxes for electroslag remelting high-carbon steels (30), such fluxes have limited application. High oxidizing capacity, low desulfurizing ability (30), and enhanced directional

solidification of the ingot (52) have been cited as advantages for these fluxes. However, as mentioned previously, the reaction of CaF_2 with SiO_2 forms gaseous SiF_4 which contributes to undesirable ingot porosity and process instability. If easily oxidizable elements are present in the metal, oxidation will occur when SiO_2 -containing fluxes are used. This oxidation involves an exchange reaction which increases the silicon content of the metal. Typical flux compositions contain 5 to 15 weight-percent SiO_2 , 15 to 30 weight-percent CaO , and 50 to 80 weight-percent CaF_2 (48).

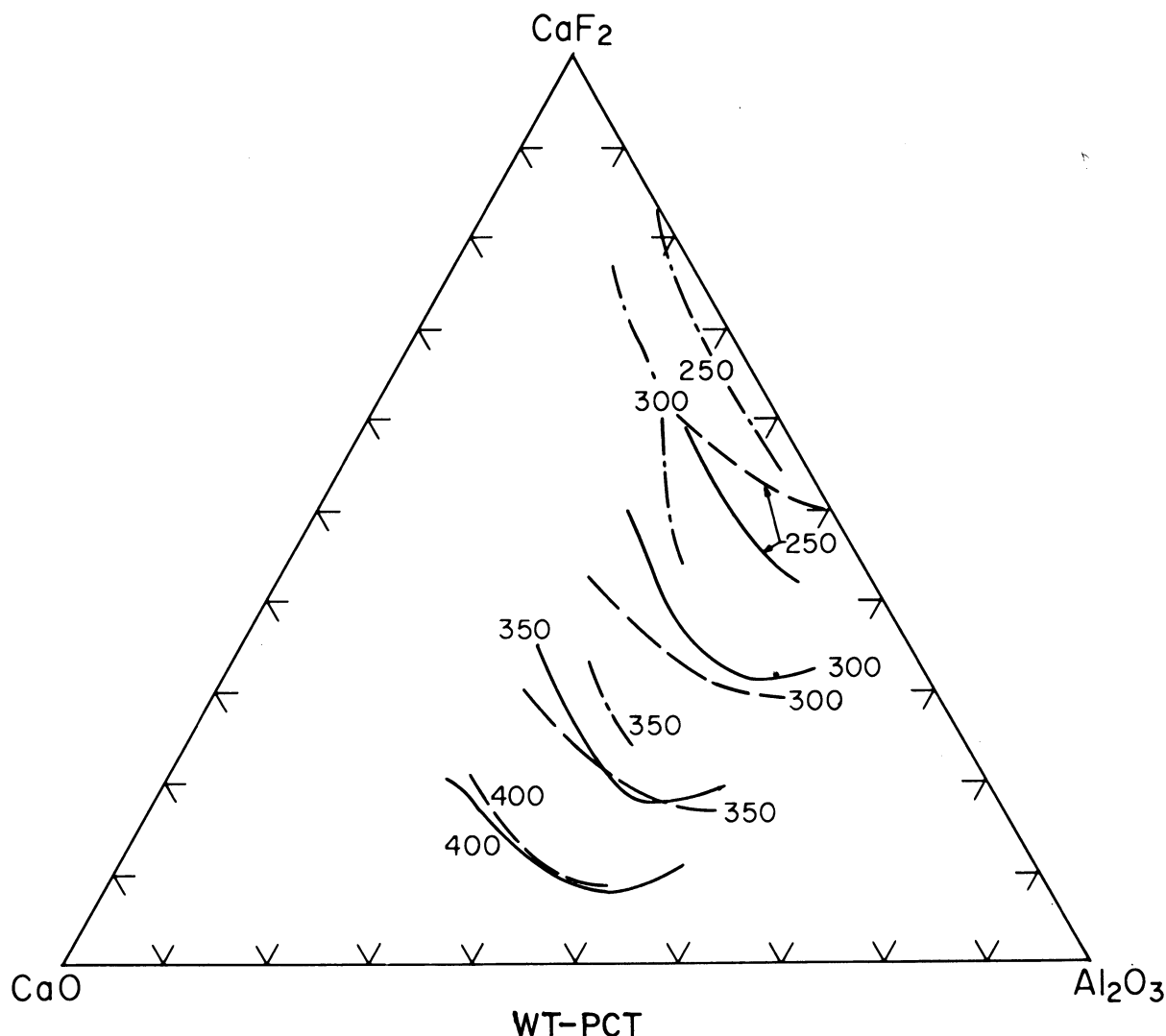


Figure 41.—Surface tension (erg cm^{-2}) as a function of flux composition in the system CaF_2 - CaO - Al_2O_3 at $1,550^\circ\text{C}$ (solid curves), $1,600^\circ\text{C}$ (dot-dashed curves, 17), and $1,700^\circ\text{C}$ (dashed curves, 45).

Equilibrium phase relations for the CaF_2 - CaO - SiO_2 system have been determined by numerous investigators (1, 16, 19, 37). Each of four binary calcium silicates is stable at liquidus temperatures up to approximately 50 weight-percent CaF_2 . Above this, CaF_2 is the stable primary phase. An extensive liquid immiscibility region extends from approximately CaO -70 weight-percent SiO_2 to SiO_2 -80 weight-percent CaF_2 . Mukerji (37) determined that the CaF_2 - CaO - $3\text{CaO}\cdot\text{SiO}_2$ and CaF_2 - $3\text{CaO}\cdot\text{SiO}_2$ - $2\text{CaO}\cdot\text{SiO}_2$ ternary eutectics have liquidus temperatures and compositions of $1,106^\circ\text{C}$ and 36CaF_2 - 52CaO -

12SiO_2 (weight-percent) and $1,104^\circ\text{C}$ and 43CaF_2 - 42CaO - 15SiO_2 (weight-percent), respectively, whereas Hillert (19) determined the solid phase assemblages present at the two ternary eutectics in the same region to be CaO - $3\text{CaO}\cdot\text{SiO}_2$ - $2\text{CaO}\cdot\text{SiO}_2$ [$1,250^\circ\text{C}$ liquidus temperature and 31CaF_2 - 55CaO - 14SiO_2 (weight-percent) composition] and CaF_2 - CaO - $2\text{CaO}\cdot\text{SiO}_2$ [$<1,180^\circ\text{C}$ liquidus temperature and 40CaF_2 - 47CaO - 13SiO_2 (weight-percent) composition].

The addition of up to 15 weight-percent SiO_2 increases the density of molten fluxes in the CaF_2 - CaO - SiO_2 system from 2.52 for CaF_2 to

2.63 gm cm⁻³ at 1,450° C (53). This slight increase is believed due to the formation of complex ions in the liquid. This suppresses the greater density increase when CaO alone is added to CaF₂ (fig. 31).

CaF₂-Al₂O₃-TiO₂

Latash and Medovar (30) have reported the use of a 50CaF₂-25Al₂O₃-25TiO₂ flux (ANF-21) for electroslag melting steel containing titanium and for limiting sulfur removal. Bhat (2) used a 70CaF₂-20Al₂O₃-10TiO₂ flux for electroslag melting maraging 18-percent nickel steel. The electrical conductivity of the Soviet flux increases from 1.8 ohm⁻¹ cm⁻¹ at 1,400° C to 3.6 ohm⁻¹ cm⁻¹ at 1,900° C (30). Hillert (19) determined that liquidus temperatures decrease along the CaF₂-TiO₂ boundary curve from 1,365° C at the CaF₂-TiO₂ binary eutectic to 1,280° C at 10 weight-percent Al₂O₃.

CaF₂-Al₂O₃-Na₂O

Nikitin, Ershov, and Malinovskii (39) conducted electroslag melts of chrome steels using 5 weight-percent Na₂O additions to CaF₂-Al₂O₃ fluxes. Smooth ingot surfaces were obtained as well as a high degree of desulfurization. Decreased flux viscosity improved the heat transfer in the molten bath. Latash and Medovar (30) reported that the electrical conductivity of such fluxes increased from 2.5 ohm⁻¹ cm⁻¹ at 1,400° C to 5.4 ohm⁻¹ cm⁻¹ at 1,900° C.

QUATERNARY AND HIGHER ORDER OXYFLUORIDE SYSTEMS

CaF₂-CaO-MgO-Al₂O₃

Two compositions in this quaternary system have been used extensively as fluxes in the electroslag process. Soviet investigators have used a composition of 18CaF₂-25CaO-17MgO-40Al₂O₃ (AN-291) to melt certain structural steels into good, workable ingots (30). Bhat (2) used a composition of 30CaF₂-17CaO-13MgO-40Al₂O₃ with a stated liquidus temperature of 1,320° C ± 10° to melt René 41 and maraging 18-percent nickel steel. This flux composition has been patented by Bhat and Tobias (3) for electroslag melting nickel-base superalloys as well as ferrous alloys. Fluxes in the system CaF₂-CaO-MgO-Al₂O₃ are claimed to provide melt rates 32 percent higher, with a decrease in energy consumption of 25 percent, compared with a 70CaF₂-30Al₂O₃ flux (22). Ingot quality of bearing steel was comparable with either flux. Latash and Medovar (30) stated that the AN-291

flux possesses a large melting interval, but no systematic studies of either liquidus and solidus temperatures or primary phases have been conducted. This is the subject of work in progress at the Albany Metallurgy Research Center.

Since there is less CaF₂ in the aforementioned quaternary fluxes compared with commonly used binary and ternary oxyfluoride fluxes, the electrical conductivity is lower while viscosities are generally higher. For the AN-291 flux, conductivities range from 0.3 ohm⁻¹ cm⁻¹ at 1,400° C to 1.7 ohm⁻¹ cm⁻¹ at 1,600° C (30). Viscosities decrease from 1.25 poises at 1,500° C to 0.65 poise at 1,700° C. Bhat and Tobias (3) state that viscosities of 0.1 to 0.01 poise apply to the 30CaF₂-17CaO-13MgO-40Al₂O₃ at temperatures of interest in the electroslag process.

Other Systems

Several polycomponent oxyfluoride fluxes which were developed by Soviet investigators for electroslag welding applications (44) served as logical fluxes for early experiments in electroslag melting. Compositions of these fluxes, together with others developed subsequently, are listed in table 12. Robinson and Grainger (47) electroslag-melted mild steel with the AN-22 flux in early experiments. Sound ingots with rough surfaces were obtained. No desulfurization, some oxidation, and increases in silicon in the ingots were noted. Later, these authors began using more conventional fluxes currently in use. The AN-25 flux was initially used for cold starts because of its high conductivity in the solid state. Subsequently, unspecified exothermic compounds were used to minimize titanium nitride contamination in the metal (30).

Since the fluxes in table 12 have limited use in the electroslag process and systematic studies of relevant systems would be extremely complex, available data on liquidus temperatures, primary phases, and physicochemical properties are sparse. Massazza and Pezzuoli (32) studied solid state reaction at 1,300° C in the system CaF₂-CaO-Al₂O₃-SiO₂ and found seven complex phases. Nikitin and Pyatnitsa (38) presented the liquidus surface of a portion of the CaF₂-CaO-Al₂O₃-SiO₂ system based on theoretical calculations and observations on fluxes after electroslag melting. The resulting diagram is characterized by 28 primary phase volumes, 48 boundary surfaces, 60 boundary curves, and at least 36 invariant points.

Scattered data on physicochemical properties of polycomponent fluxes in the systems CaF₂-

Table 12.—*Polycomponent oxyfluoride fluxes for the electroslag process*

Designation	Composition, wt-pct								Uses	Ref.
	CaF ₂	CaO	MgO	Al ₂ O ₃	SiO ₂	TiO ₂	MnO	Fe ₂ O ₃		
ANF-6 ^{1,2}	64	6	0	22	3	0	0	0	Steels	
X1AA ³	60	10	0	26	4	0	0	0	Experimental	2
X2AA ³	60	20	0	17	3	0	0	0	 do.	2
None	30	30	0	30	10	0	0	0	High-carbon tool steels ..	49
Y4A ³	40	0	10	43	7	0	0	0	Experimental	2
None	30	0	10	40	20	0	0	0	Tool steels (Hopkins flux)	49
Y2A ³	30	0	10	34	26	0	0	0	 do.	2
TIC ³	50	0	0	34	4	12	0	0	 do.	2
None	80	10	0	5	0	5	0	0	 do.	2
ANF-14 ¹	60	10	10	10	10	0	0	0		
None	55	15	3	25	2	0	0	0	Hot work die steels	49
Y3A ³	30	17	13	34	6	0	0	0	René 41	2
None	75	10	5	5	0	5	0	0	Experimental	2
None	35	15	5	0	10	35	0	0	Conductive, cold start	49
AN-5 ¹	5	25	15	0	55	Trace	0	0		
AN-10 ¹	20	10	0	20	20	0	30	0		
AN-22 ¹	20	15	15	20	20	0	10	0	General purpose, electro-slag welding	47
AN-8 ¹	13-19	4-7	5-7	11-15	33-36	0	21-26		 do.	44
AN-25 ¹	30-40	12-15	2-4	0	5-10	40	0	5	Conductive, cold start	44

¹ Soviet designation.² Composition of a typical 70CaF₂-30Al₂O₃ flux after electroslag melting.³ Designation of Bhat (2).

CaO-Al₂O₃-SiO₂ and CaF₂-CaO-MgO-Al₂O₃-SiO₂ show that Al₂O₃ and SiO₂ have the greatest effect in reducing electrical conductivity at a given temperature because of complex anion formation. At 1,400° C, the ANF-14 flux has a specific electrical conductivity of 1.86 ohm⁻¹ cm⁻¹ (10). A composition approximating ANF-6 yields a conductivity value of 1.42 ohm⁻¹ cm⁻¹ at the same temperature (10). An inverse relationship between viscosity and electrical conductivity ex-

ists for CaF₂-CaO-Al₂O₃-SiO₂ fluxes. Viscosities range from 0.16 poise for a composition of 87CaF₂-2CaO-2Al₂O₃-9SiO₂ (24) to 2.5 poises for a composition of 7CaF₂-35CaO-21Al₂O₃-37SiO₂ (23).

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R. L. Lincoln and N. Riazance of the Albany Metallurgy Research Center conducted many of the thermal analysis experiments in the system CaF₂-CaO-Al₂O₃.

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⁴ Titles enclosed in parentheses are translations from the language in which the item was published.

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CHAPTER 7.—ELECTROSLAG MELTING OF TITANIUM AND ALUMINUM¹

By R. H. Nafziger, R. A. Beall,² S. L. Ausmus,³ and J. T. Dunham⁴

In the late 1950's, reports were received from the Soviet Union concerning experiments in submerged arc welding of titanium using a flux. With this as a basis, the production of titanium ingots by the electroslag process evolved at the E. O. Paton Electric Welding Institute in Kiev. Morozov and coworkers (9) were among the first to report results. The Soviets were particularly interested in utilizing the electroslag process to obtain slab-shaped titanium ingots from which to roll sheet. Ingots with smooth, directly workable surfaces and better yield were obtained. Furthermore, expensive dc rectifiers were not required. These factors encouraged the Soviets to explore the possibilities of electroslag melting of titanium and evaluate its potential compared with that of vacuum-arc melting. Prefused and dried alkaline-earth fluorides (except magnesium fluoride) were the fluxes used. It was concluded that no particular fluoride possessed marked advantages over others, so the cheaper CaF_2 was preferred. The laboratory furnace was evacuated to 10^{-2} torr and backfilled with 1.1 atm of argon. Single-phase ac was the power supplied. Mechanical properties (tensile and impact strength, elongation, and reduction in area) of electroslag- and vacuum-arc-melted titanium were compared and found to be nearly equal except that electroslag-melted metal had slightly lower impact strength. Somewhat later, Gurevich and coworkers

(5-6) produced 13-cm (~ 5 -inch) diameter round and 7.5- by 17.5-cm (~ 3 - by 7-inch) slab technical-grade titanium and titanium alloy ingots by the electroslag process with CaF_2 using the same procedure as described above. Single melts were deemed sufficient when flat, extruded electrodes made from titanium sponge were used. Mechanical properties (ductility and impact strength) compared favorably with those of double-vacuum-arc melted material. Recent Soviet advances in electroslag melting titanium include melting in an open movable mold which produces ingots similar in hardness and mechanical properties to the electrode, indicating minimal contamination (10).

Such reports interested the U.S. Air Force, and subsequently, Mellon Institute of Carnegie-Mellon University of Pittsburgh was provided funds to show (1) the feasibility of producing large titanium and titanium alloy ingots by the electroslag process, (2) the feasibility of producing titanium slabs from nonwelded electrodes, and (3) the economy that could be effected by electroslag melting to produce ingots with smooth surfaces which, in turn, would reduce the number of mill operations. Single ac electroslag melts under an inert atmosphere were successful in preparing titanium and Ti-6Al-4V alloy ingots. A proprietary method of producing the electrodes and a bottom molten-flux start were employed (3).

In the light of the aforementioned Soviet reports, personnel from the U.S. Army Materials and Mechanics Research Center, Watertown, Mass., contacted the Bureau of Mines, and research on this subject was initiated at the Albany Metallurgy Research Center in 1965. The stated objective was to develop a process to produce slab-shaped titanium ingots, with the understanding that the Soviet claims for the electroslag process would be evaluated.

¹ Adapted from Trans. Internat. Vacuum Metallurgy Conf., 1967, ed. by E. L. Foster, ed., Am. Vacuum Soc., New York, 1968, pp. 675-694; Proc. 1st Internat. Symp. on Electroslag Consumable Electrode Remelting and Casting Technology, Pittsburgh, Pa., 1967, pt. 1; Topical Reports to U.S. Army Materials and Mechanics Research Center, Watertown, Mass., USBM-RC-1262, 1966, and USBM-RC-1351, 1969; Trans. Am. Foundrymen's Soc., v. 77, 1969, pp. 353-359; Proc. 2d Internat. Symp. on Electroslag Remelting Technology, Pittsburgh, Pa., 1969, pt. 1.

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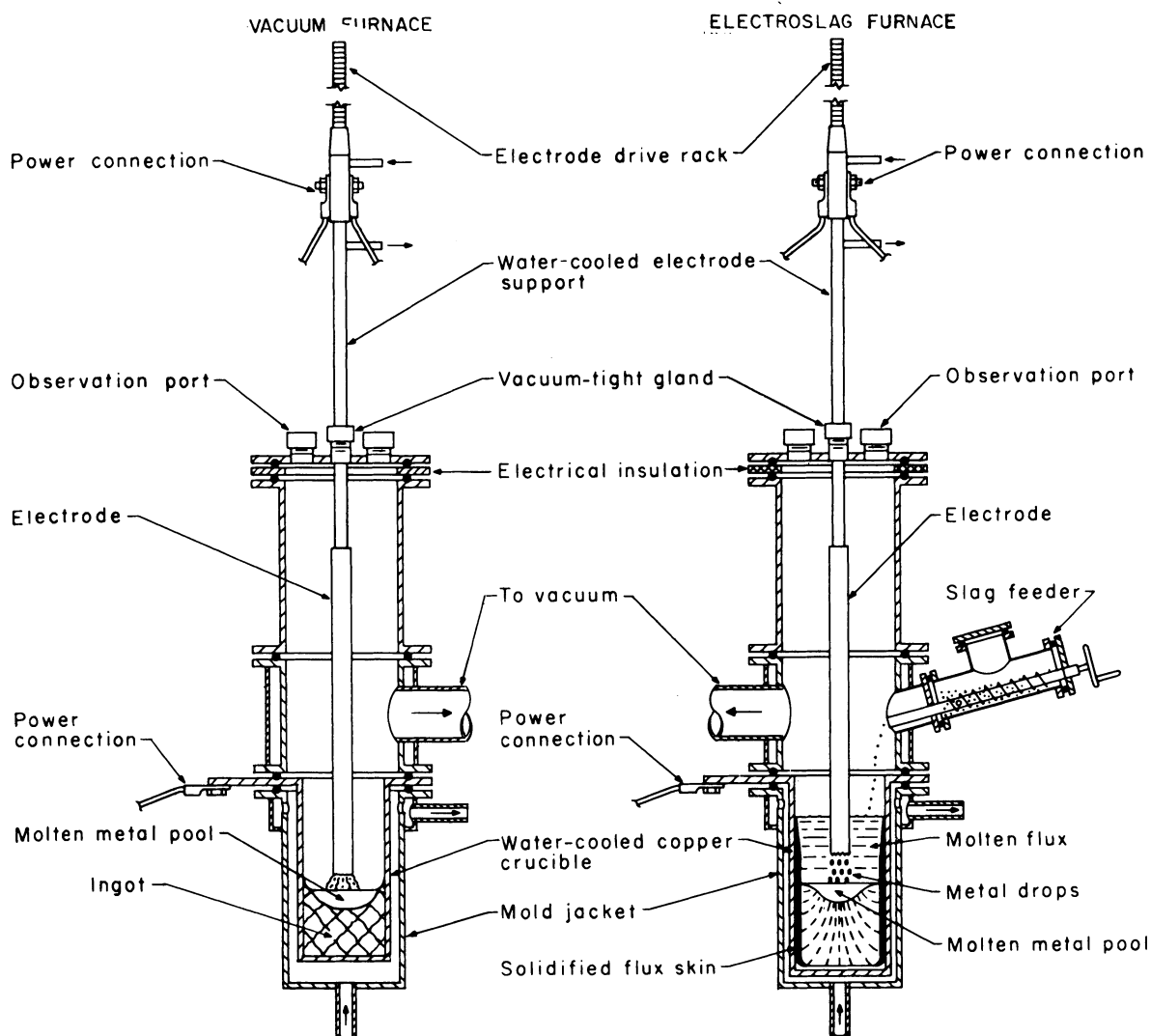


Figure 42.—Schematic drawings of vacuum-arc and electroslag furnaces.

The benefits hoped for from electroslag melting of titanium included (1) improved directionality of cooling, (2) controlled and slower melt rate, (3) shallower pool and more even heat distribution across the pool, (4) reduction in segregation as a result of fine grain size and shallow thermal gradients, (5) improved ingot sidewall, and (6) reduction in loss of volatile alloy components.

EQUIPMENT

For electroslag melting research, a conventional cold mold arc melting furnace was first modified to include a feeder to allow manual side feed of slag during melting. Figure 42 com-

pares a vacuum-arc furnace with a furnace modified for electroslag melting. A slab-shaped water-cooled crucible 9.2 by 17.5 cm ($3\frac{5}{8}$ by $6\frac{7}{8}$ inches) at the top, tapered to 7.6 by 16.2 cm (3 by $6\frac{3}{8}$ inches) over a 26.4-cm ($10\frac{3}{8}$ -inch) depth, was prepared. Conventional 10.2- to 12.7-cm (4- to 5-inch) round water-cooled crucibles were also used.

In a later version of the furnace, the side feeder was eliminated and dry slag was charged into the furnace before initiation of melting. The crucibles were cooled during melting with water flowing at approximately 50 gal min⁻¹ under 2.11-kg cm⁻² (30-psi) pressure.

For both electroslag and vacuum-arc melting, the electrode was fed into the crucible by manually energizing a small brake-motor drive unit. The rate of electrode feed was regulated by monitoring the ampere and volt meters.

The vacuum system for evacuating the furnace was a conventional mechanical pump having a free air capacity of 50 liters min^{-1} . Adequate evacuation was considered to be met with 50 microns pressure, which was achieved with a maximum leak rate of 5 microns min^{-1} . Generally, the leak rate was less. For vacuum-arc melting, a dynamic vacuum was maintained throughout melting. For electroslag melting, the furnace was evacuated, isolated from the pump, and backfilled to a partial pressure of helium, usually to $\frac{1}{3}$ atm.

When melting with dc power, the furnace was connected to the main power supply of the melting laboratory. This power supply consisted of a parallel bank of air-cooled welding rectifiers (selenium) of 1,000 amperes capacity each. The total capacity of the bank was over 15,000 amperes at 35 volts. The open circuit potential was 70 volts. Power was controlled by a saturable reactor for the individual rectifiers. As a group, the power was controlled by switching the units in or out of the circuit. The furnace could be connected to the power supply for either straight-polarity (electrode negative) or reversed-polarity melting.

The single-phase ac power supply consisted of three welding transformers connected in parallel. Rated capacity of each transformer was 1,500 amperes at 45 volts. Open circuit potential was 90 volts. Power control was by manually controlled motor-driven movable cores in the transformers.

In dc melting, Faradaic reactions occur at the electrode-flux and ingot-flux interfaces. These reactions must be accounted for when considering the transfer of ionic species between the various phases. These reversible reactions occur quickly in ac melting, and reactance and power factor problems must also be considered.

Other equipment included a hydraulic press for briquetting sponge into compacts and a tank for welding the compacts into electrodes. All welding on titanium was done in the welding tank with a nonconsumable thoriated tungsten electrode under a backfilled atmosphere of helium.

MATERIALS

Sponge

Titanium sponge is not a uniform material as far as the products of the several sources are concerned, and a melting process suitable for one type is not necessarily suitable for all types of sponge. For instance, one firm utilizes a magnesium reduction of TiCl_4 to form sponge which is subsequently leached with an aqueous solution and then dried. Magnesium chloride is more likely to be trapped or occluded in this type of sponge. Another firm reduces the tetrachloride in two steps with sodium and leaches the resultant sponge, producing finer particle sizes than those in magnesium-reduced sponge. Hydrogen is also somewhat lower. A third producer depends on a magnesium reduction followed by either a gas-sweep system, a water leach, or both. Imported sponge is usually magnesium reduced and purified in vacuum to remove excess magnesium and chlorides. Hydrogen content is lower in imported sponge than in domestic material. Electrolytic titanium, which may be used in place of sponge, is now available on the market for a premium price. The sponge source is a significant factor, since electroslag melting does not remove hydrogen, excess reductant, and volatile salts as does the vacuum-arc process.

The sponge electrodes were prepared for melting by briquetting 25.4-cm-long rectangular bars, generally ~ 5 by 5 cm (2 by 2 inches) in cross section at 2,110 kg cm^{-2} (30,000 psi) and butt-welding the bars together. The density of the briquetted bars was 3,875 kg m^{-3} (0.14 lb in^{-3}). The bars or electrodes were stored in a drying oven at 66° C until charged into the melting furnace.

Fluxes

The limitations on the choice of flux compositions for electroslag melting titanium have been discussed in chapter 5. It was concluded that no single flux composition is ideal from the standpoint of all the considered parameters.

Small amounts of reducing agents have been added to CaF_2 fluxes in an effort to remove oxygen from the molten metal during melting. In addition, relatively volatile constituents have been added to CaF_2 fluxes to evaluate their potential as sweeping agents to remove or reduce gaseous impurities from the molten metal. Selected binary and ternary compositions of alkaline-earth and lanthanum fluorides have also been used as slags for melting titanium. The

following flux compositions have been used, based on the considerations noted in chapter 5:

1. CaF_2 , reagent, acid-grade, native fluorspar.
2. Additions to CaF_2 :
 - 1, 3, 5, weight-percent C.
 - 2, 5 weight-percent Y.
 - 3 weight-percent Gd.
 - 5 weight-percent K_2TiF_6 .
 - 5, 7.5, 10, 20, 23, 30, 58 weight-percent CaCl_2 .
 - 18.5 weight-percent SrF_2 .
 - 4, 12 weight-percent MgF_2 .
 - 4 weight-percent MgF_2 -50 weight-percent LaF_3 .
 - 1 weight-percent C-9 weight-percent MgF_2 .
 - 20, 52, 75 weight-percent LaF_3 .
3. MgF_2 .
4. Addition to MgF_2 : 20 weight-percent LaF_3 .
5. LaF_3 .
6. BaF_2 .

Morozov and coworkers (9) have demonstrated that titanium ingots produced with untreated CaF_2 flux are unsatisfactory with respect to impurities and mechanical properties. Although as-received flux impurity contents vary according to lot, Al, Cr, Fe, Mg, and Si are present ranging from 30 parts per million (ppm) up to 3 percent in as-received CaF_2 and MgF_2 . A few parts per million of magnesium and silicon were the only impurities observed in untreated LaF_3 . Up to 0.59 percent CO_2 and considerable moisture were present in as-received CaF_2 . It was therefore evident that some method of heat treatment of the flux was required before use. The flux was isostatically pressed, crushed, and heated in air at 600° to 650° C for approximately 2 hours. This initial heating removes enough moisture to prevent HF from forming or contaminating the furnace and vacuum lines in the subsequent fusion.

Flux fusions at 1,420° to 1,450° C for CaF_2 were conducted either in a graphite resistor furnace or in water-cooled copper crucible using a nonconsumable titanium electrode. The latter method permitted up to 7 kg of material to be fused at one time. Fluxes were fused in the resistor furnace in a graphite crucible with and without a TZM alloy (Mo-0.5 weight-percent Ti-0.8 weight-percent Zr-0.015 weight-percent C) liner, and titanium chips were added in an effort to getter impurities. Figure 43 shows a typical CaF_2 fused billet together with the liner and graphite crucible.

Present studies show that the concentrations of Al, CO_2 , and Si in the fused flux are independent of the type of fusion and the flux composition. Reductions in Fe, Mg, and C are observed when a liner and no titanium are used in

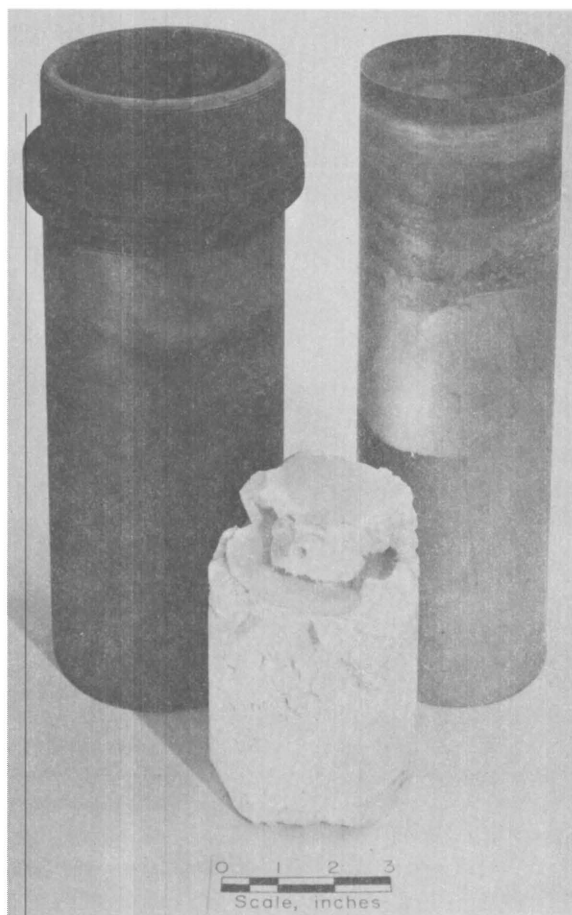


Figure 43.—Reagent-grade CaF_2 flux billet (front) after fusion in the graphite resistor furnace. Graphite crucible (left) and TZM liner (right) are also shown.

the resistor furnace. Under the conditions of fusion, it appears that the titanium chips do not act as effective impurity getters. For example, flux impurity levels in ppm after fusion without a liner were as follows: Al 155, 450; C 170, 608; CO_2 75, 179; Fe 100, 139; Mg 1,000, 763; Si 440, 480; and Ti 750, 3,320. (The first value in each case represents the impurity level obtained without titanium chips and the second value that obtained with titanium chips.) Under the conditions of fusion, therefore, it appears only a TZM alloy liner is needed for treating fluxes in the resistor furnace.

Experience has shown that approximately one-half of the tested flux compositions mentioned previously give satisfactory operating conditions. The observed degassing during runs employing MgF_2 is due to the less stable nature of this com-

pound at operating temperatures. Owing to the slight density differential between flux and metal, LaF_3 tends to become entrapped in the metal. The best operating conditions were obtained with CaF_2 flux. Either acid- or reagent-grade CaF_2 may be used. Used CaF_2 top flux can be reused without further treatment.

Reuse is important from the standpoint of the economics of the electroslag process. Used top flux of this composition does not increase in impurity level over that of the originally fused material (table 13). Used sidewall flux, however, is contaminated sufficiently to preclude its further use. Calcium fluoride fluxes may also be recycled (used flux crushed and fused again prior to electroslag melting) at least once without adversely affecting the impurity concentrations.

MELTING PROCEDURES

After the electrodes and fluxes are prepared, the fused hot flux is loaded either into the flux feed mechanism or directly into the furnace around the electrode. A basal charge of titanium metal sponge, turnings, or chopped scrap is placed in the melting crucible beneath the flux. The electrode is fixed to the furnace electrode shaft and positioned for adequate clearance, and the system is closed and evacuated. When the system has been evacuated to ~ 50 microns of pressure, helium gas is backfilled into the furnace, and the unit is ready for melting operations.

An arc is initiated between the electrode tip and the basal charge, and power is raised until a full molten pool is established. At that time flux feed begins, and flux material is fed in as rapidly as possible to totally submerge the melting zone.

Alternatively, an arc is struck and the charged flux is melted at power levels low enough not to consume the electrode.

When the flux in the furnace becomes molten, the system clears of most of the initial smoke. Potential drops when the flux becomes molten and may be as low as 27 to 28 volts. Melting continues at a predetermined current until the total electrode charge is consumed.

There is evidence that once the salt bath has become molten and the electrode tip submerged beneath the molten surface, the melting takes place by resistance heating of the electrode by means of the superheated flux. This assumption is based on the following observation: examination of the tips from deeply submerged electrodes reveals that these are acutely tapered from a point on the electrode corresponding to the flux pool surface to a rather sharply rounded point about 1.3 to 1.9 cm ($\frac{1}{2}$ to $\frac{3}{4}$ inches) above the molten metal surface. This latter spacing is governed by the operating voltage. Melting is observed to take place from the surface of the flux pool downward.

A second observation supporting these assumptions is that sudden massive additions of cold flux made during a melt invariably result in interruptions of steady-state melting conditions. Folds which correspond to these additions can be seen in the sidewalls of the ingots. These folds result when the flux pool is suddenly cooled, permitting the titanium to freeze in from the sidewall. At the same time, metal consumption ceases, and the metal pool likewise begins to freeze. Consumption resumes when the newly added flux is melted and the flux pool regains its former temperature.

Table 13.—Typical analytical data for one lot of reagent-grade CaF_2 ¹
[all numerical values given in percent impurities]

Impurity	Fused slag	Used flux		Reused flux	
		Top	Sidewall	Top	Sidewall
Aluminum	0.01–0.1	0.017	0.024	0.019	0.059
Carbon	ND	.006	.008	.003	.019
Carbon dioxide	.033	.01	.02	.04	.01
Copper	(²)	(²)	0.0003–.003	0.0003–.003	0.0003–.003
Iron	.001–.01	<.001	.006	.002	.002
Magnesium	.3–3	.05	.21	.05	.11
Molybdenum	.003–.03	0.01–.1	.001–.01	.003–.03	1–10
Silicon	.03–.3	.014	.009	.006	<.002
Titanium	3–30	.20	.07	.10	.10

ND—Not determined.

¹ range of values indicates qualitative spectrographic analysis.

² Not detected.

This is not to say that an arc cannot or does not occasionally exist. When the slag cover is insufficiently deep or when the electrode is extracted above the molten pool, arc conditions can be observed to occur even in the presence of molten flux. This is not, however, ideal, for it defeats the obvious advantages of flux melting; namely, controlled and lower melt rate and uniform heat distribution in the molten metal pool.

Operating current and potential can be varied to that appropriate for the electrode and crucible size and desired consumption rate. Typically for an ingot size of 8.9 by 16.5 by 25.4 cm ($3\frac{1}{2}$ by $6\frac{1}{2}$ by 10 inches), nominal potential is 27 to 35 volts and current is 3,000 to 3,500 amperes. Somewhat lower potentials (24 to 27 volts) are possible and practical with deeper slag covers, and potentials as high as 40 volts have been recorded. High voltages, indicating greater electrode-metal pool separation, generally result in high electrode consumption rate; conversely, low voltages result in a more uniform and lower melt rate.

It is possible to shorten the electrode-to-metal-pool spacings, and thus lower the potential to a point at which consumption ceases. Under these circumstances the flux remains molten but the system appears to be static. Consumption may be reinitiated by (1) increasing the current or (2) raising the potential. These observations all indicate that the melting rate is directly related to the watts dissipated. Furthermore, the resultant flexibility of control of melting rate is a principal merit of the technique.⁵

As would be expected, power requirements and melting efficiencies for electroslag melting differ from those encountered in conventional vacuum-arc melting. The amount of difference has not been fully established, but generally speaking, consumption rates for electroslag melts are 10 to 50 percent below those for vacuum-arc melts for a given power input.

Consumption rates for slag melts of slab-shaped ingots varied between 0.6 kg min^{-1} and about 1.5 kg min^{-1} . Power requirements per kilogram of metal (heat efficiency) vary inversely with the consumption rate so that for a consumption rate of 0.6 kg min^{-1} , power requirements are about 3.4 kwhr kg^{-1} , and for a consumption rate

of 1.5 kg min^{-1} , power requirements are reduced to 1.3 kwhr kg^{-1} .

Slab-shaped ingots melted under the optimum conditions appeared equivalent to round ingots in surface quality. Because round ingots were easier to prepare, they were used in most of the small-scale work.

Four-inch round ingots were prepared with slag depths ranging from 3.8 to 5.1 cm ($1\frac{1}{2}$ to 2 inches) deep, with currents of 4,500 to 4,800 amperes, and a potential of 20 to 23 volts. Ingot surfaces were excellent. For this size ingot, best ingot sidewall surfaces were obtained with the slag cover depth between 3.8 to 5.1 cm, a current of 4,500 amperes, and a potential of 20 to 22 volts.

RESULTS

Ingot Quality

Figures 44 to 48 illustrate titanium ingots melted under a variety of flux compositions and one vacuum-arc-melted ingot for comparison. In figure 45 the metal was melted under reagent-grade CaF_2 flux and forms a basis for comparison with the ingots in succeeding figures. This ingot possesses a smooth sidewall with a minimum of folds and should be readily forgeable. Figure 46 demonstrated that in the absence of CaF_2 in the flux, the ingots obtained are significantly inferior with respect to sidewall and entrapped flux. The ingots shown are sound except for the ingot on the right, which was melted with LaF_3 and allustrates the effect of the adverse density differential between flux and metal. This flux composition was tested to evaluate the effect of the greater high temperature stability of this composition on ingot impurity levels without regard to ingot quality so that perhaps other comparably stable rare earth fluorides with more favorable high-temperature densities might be used. Figure 47 illustrated the greater effect on sidewall quality of small additions of a more volatile and less stable component (MgF_2) to CaF_2 (left and center ingots) and the manner in which the addition of LaF_3 to such compositions results in a smoother sidewall in the melted ingot. Addition of LaF_3 to CaF_2 fluxes in various amounts produces acceptable ingots with noticeable luster, as shown in figure 48.

Ingot Chemistry

Of particular importance in evaluating the effectiveness of a flux for use in electroslag melting is its ability to remove and retain undesirable impurities. Table 14 shows impurity concentrations in ingots melted under a variety of flux

⁵ In contrast, arc potential is necessarily kept within a narrow range in vacuum-arc melting, and the melting rate is controlled by current alone. However, it is seldom possible to operate at so low a current as to stop melting because of ion population requirements to support the arc.



Figure 44.—Vacuum-arc-melted titanium ingot.

compositions using selected components listed previously. Results from vacuum-arc-melted material are shown for comparison. In all cases, magnesium-reduced, vacuum-distilled sponge was the electrode stock; the sponge analysis for com-



Figure 45.—Titanium ingot melted under reagent-grade CaF_2 flux (left) and electrode stub after melting (right).

parison is also listed in table 14. All flux melts were conducted under a static $\frac{1}{3}$ atm of helium and straight (electrode negative) dc polarity. Metallic impurities were analyzed quantitatively by optical emission spectroscopy. Carbon was analyzed by combustion, nitrogen by the Kjeldahl method, oxygen by inert gas fusion, hydrogen by hot extraction, and fluorine by specific ion-sensitive electrode method.

None of the listed impurities in table 14 are significantly affected by the indicated changes in flux composition. Electroslag melting, however, changes impurity contents in titanium with respect to vacuum-arc melting and input metal, as indicated in the table. Noteworthy are the ingot impurity levels produced when melting with three grades of CaF_2 fluxes. Initial flux impurities for reagent-grade CaF_2 were given in table 13. Table 14 shows that acid-grade CaF_2 , which sells at \$0.50 to \$0.75 per pound (\$1.11 to \$1.57/kg) is an acceptable flux substitute for reagent-grade CaF_2 , which sells at \$2 to \$4 per

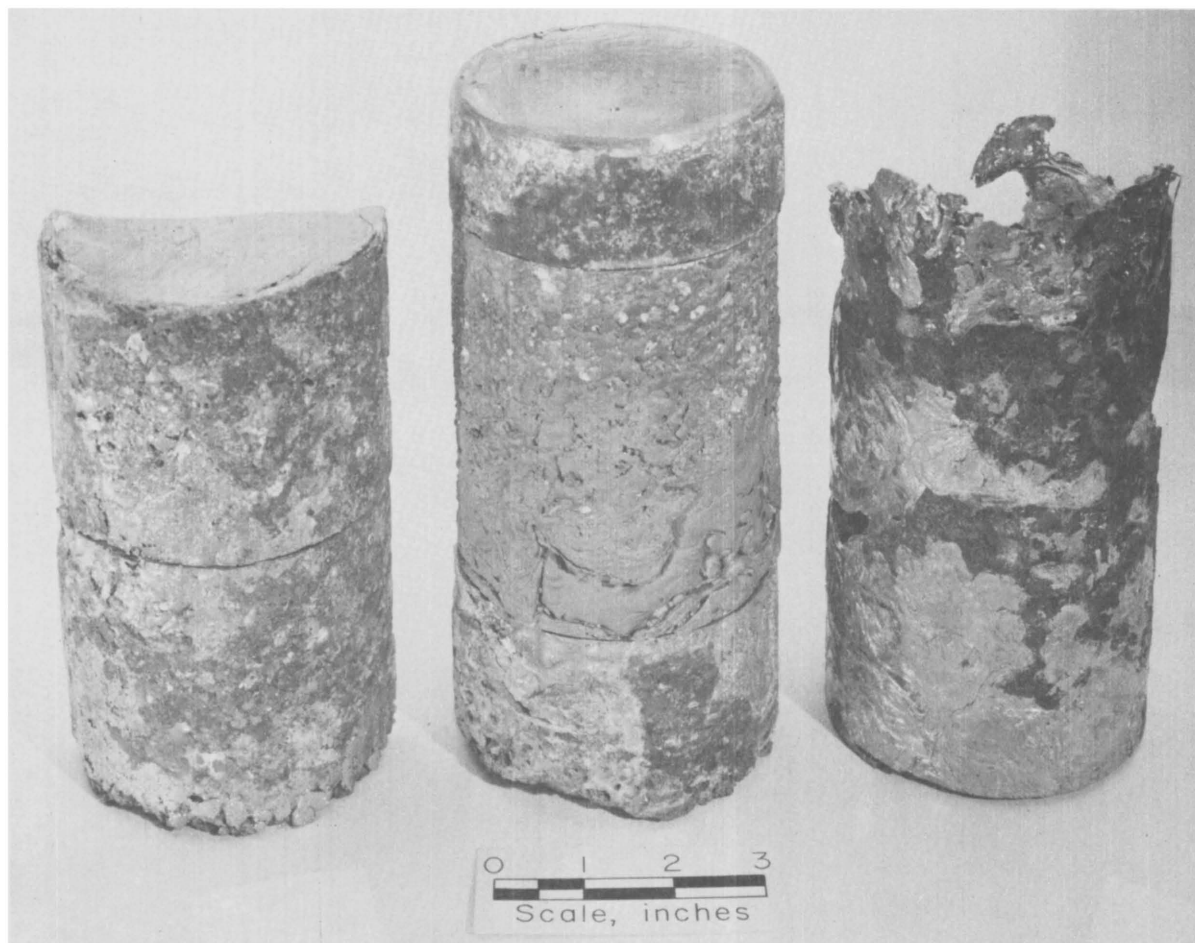


Figure 46.—Titanium ingots melted under (left to right) MgF_2 , 20 wt-pct $\text{LaF}_3\text{--MgF}_2$, and LaF_3 fluxes. Note sidewall flux adhering to ingot surfaces. Center section of center ingot has been sandblasted to remove flux. Some ingots in figures 46–48 have been cut for sampling.

pound (\$4.44 to \$8.88/kg). With the exception of ingot silicon and oxygen, the use of native fluorspar as a flux (\$0.06/lb; \$0.13/kg) produces ingot with impurity levels comparable to those produced with higher priced CaF_2 fluxes.

Table 15 presents impurity data as a function of amount and type of reducing agent added to fluoride fluxes. The melting conditions were identical to those indicated for the melts given in table 14. Carbon flux additions are shown to reduce ingot metallic impurities, especially iron; as expected, carbon contents are increased. Figure 49 illustrates three ingots melted under a 1-weight-percent carbon- CaF_2 flux, using various melting parameters which are discussed later in this chapter. The ingots are sound and possess smooth sidewalls. Sidewall flux is easily removed.

Yttrium and gadolinium additions to CaF_2 produce ingots whose impurities are not significantly reduced. In all cases, ingot oxygen contents are not decreased compared with those of ingots melted without reducing agents.

The addition of more volatile components to CaF_2 fluxes results in ingot impurity levels comparable to those obtained with fluoride fluxes having no additions. Pertinent data are shown in table 16.

In most cases, correlation coefficients (r) relating ingot impurities (Fe, Mg, Si, C, H, Y, O, N, F) with binary flux compositions were not significant at the 10-percent level. The exceptions were—

1. Ingot fluorine increases with increasing MgF_2 ($r=0.999$; 1-percent level).

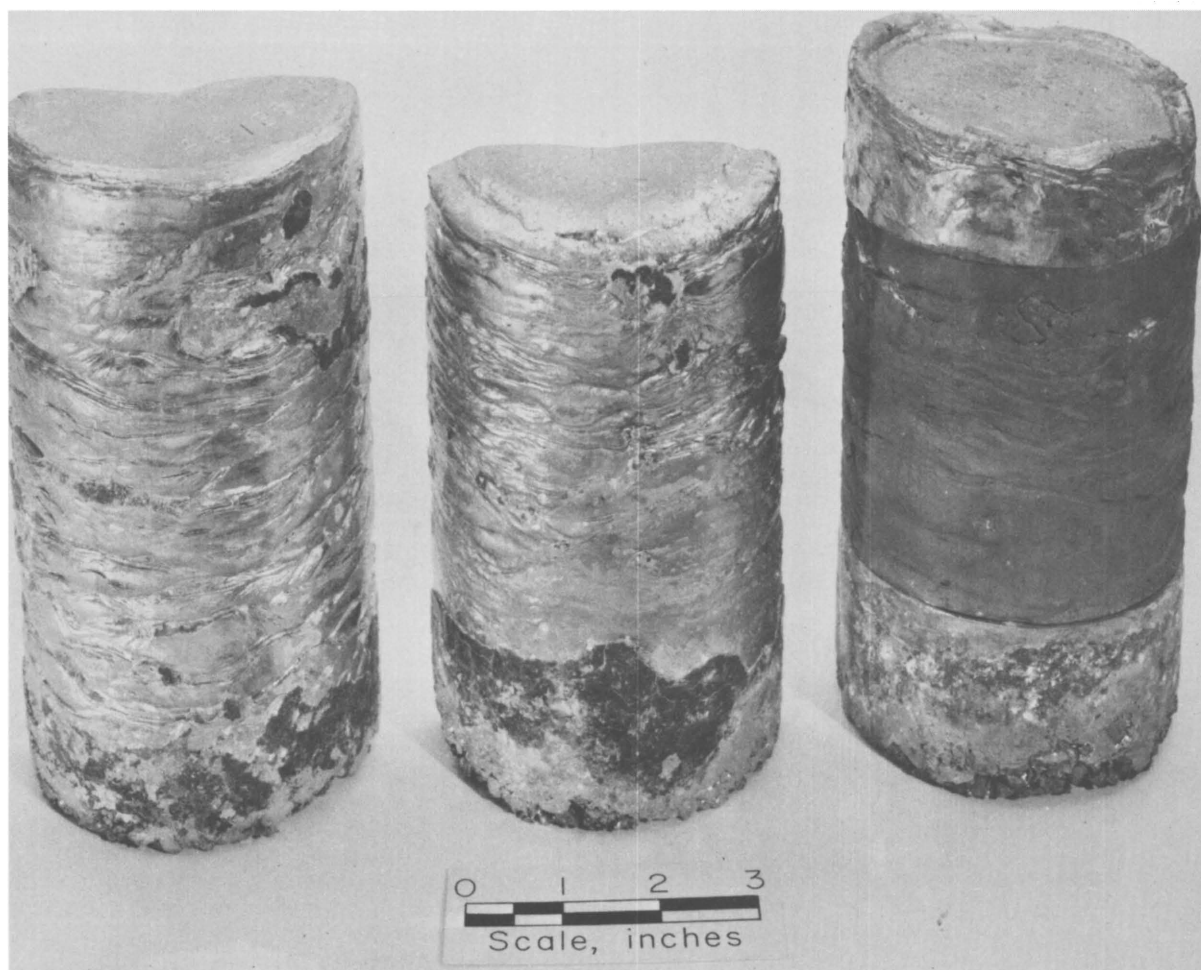


Figure 47.—Titanium ingots melted under (left to right) 4 wt-pct MgF_2 - CaF_2 , 12 wt-pct MgF_2 - CaF_2 , and 4 wt-pct MgF_2 -50 wt-pct LaF_3 - CaF_2 fluxes. Center section of ingot on right has been sandblasted to remove flux.

2. Ingot yttrium increases with increasing Y ($r=0.992$; 10-percent level).

3. Ingot hydrogen increases with increasing CaCl_2 ($r=0.931$; 5-percent level), and ingot magnesium decreases with increasing CaCl_2 ($r=0.992$; 1-percent level).

Flux-Metal Impurity Partitioning

A distribution ratio, D , of the specific impurity between the flux and metal phases is herein defined as the ratio of the impurity content of the used slag to that of the ingot. The term D' is defined as the ratio of impurity in the initial fused flux to that in the electrode. A favorable impurity partitioning between the flux and metal is thus indicated by $D' < D$ or $D'/D < 1$. Values for D'/D for the indicated impurity as a function of flux composition are given in table 17. If

$D'/D = 1$, there is no impurity migration between flux and metal, whereas if $D'/D > 1$, unfavorable impurity partitioning is indicated.

Table 17 shows that regardless of flux composition, silicon and nitrogen are generally unfavorably partitioned, although nitrogen is more favorably distributed when MgF_2 is added to CaF_2 . Lower impurity values, however, make ratio calculations more uncertain for nitrogen than for other impurities. Generally, magnesium is favorably distributed between flux and metal.

Poor partition correlation is shown with iron as a function of flux composition, and carbon is unfavorably partitioned except when pure MgF_2 or MgF_2 additions to CaF_2 fluxes are used. Favorable partitioning characterizes the distribution of aluminum except when LaF_3 and MgF_2 are used as flux additions. In nearly all of the runs

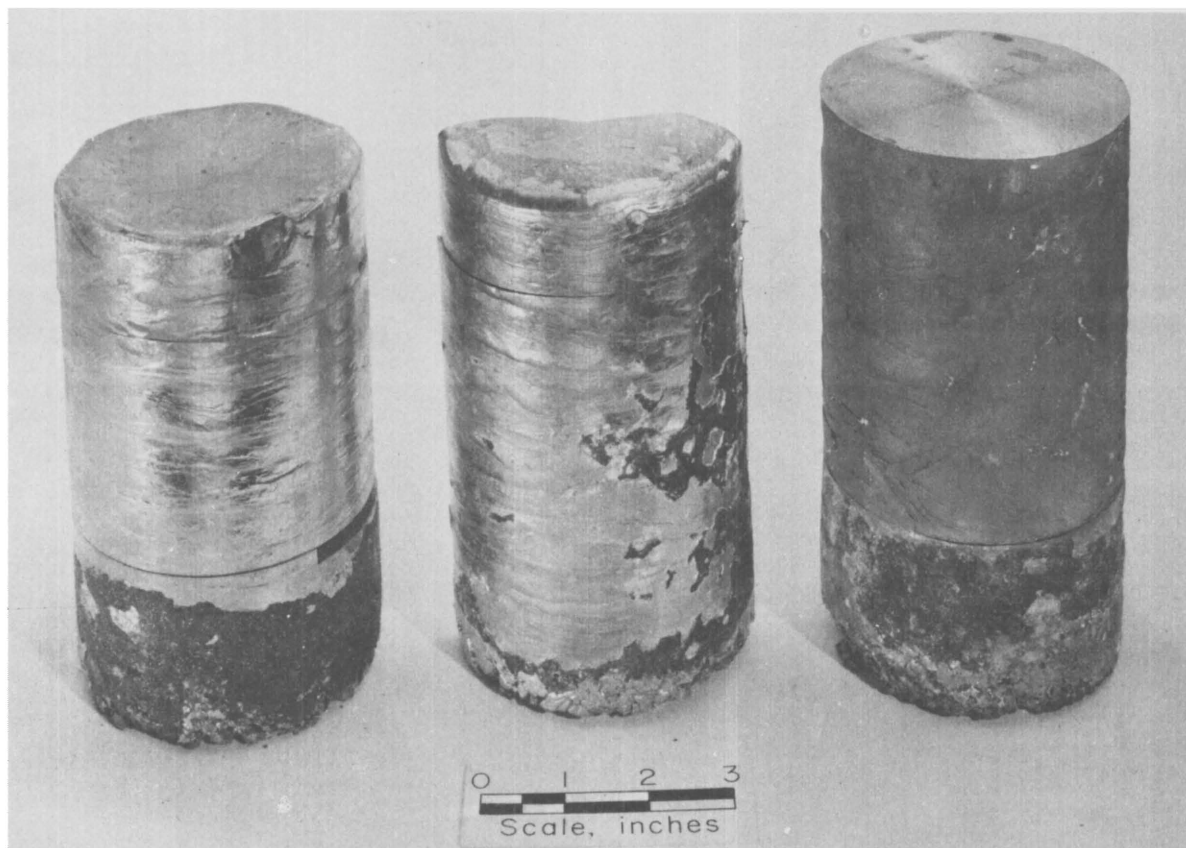


Figure 48.—Titanium ingots melted under (left to right) 20 wt-pct $\text{LaF}_2\text{--CaF}_2$, 52 wt-pct $\text{LaF}_3\text{--CaF}_2$, and 75 wt-pct $\text{LaF}_3\text{--CaF}_2$ fluxes. Top of ingot to right has been cut and machined for sampling and hardness determinations after being sandblasted to remove flux.

shown in table 17, H_2 and O_2 are not effectively removed from the metal with the exception that O_2 was removed in run SA 26198.

Additional analytical data are shown in table 18 for another series of heats. In this case, the values represent an impurity reduction in the metal to that in the electrode. Hence, values less than 1 in table 18 represent an impurity reduction in the metal after electroslag melting. Additions of CaCl_2 to the CaF_2 fluxes rendered the ingot metal somewhat harder, and these fluxes are difficult to handle owing to their deliquescent nature. In general, CaCl_2 additions do not lower impurity concentrations in the ingot metal to any substantial degree. There appears to be no correlation of impurity level with flux composition except as noted above.

Ingot Fluorine Contents

One difference between electroslag-melted titanium and that melted by vacuum arc is the

consistent presence of fluorine in the former material and its absence in the latter. Typical average fluorine analyses for electroslag-metal material are given in table 19. The uncertainties in these data are ± 50 percent. No definite conclusions can be reached regarding fluorine content as a function of flux composition except that the more stable fluoride (LaF_3) contributes less fluorine to the metal than does a less stable fluoride (MgF_2). These results are expected from thermochemical considerations.

When the consumable electrode is made the anode (positive), fluoride anions formed from the ionization of the flux apparently tend to migrate away from the negatively charged ingot which is forming. The result is a lower fluorine content in the ingot, as shown in table 19. All the heats shown in this table were conducted under static helium of $\frac{1}{3}$ total pressure except where noted. Evidently furnace atmosphere has little bearing on resulting ingot fluorine contents.

Table 14.—*Ingot impurity levels in electroslag-melted titanium as a function of fluoride-flux composition*

Flux composition	Ingot impurity, ppm ¹										
	Al	Cu	Fe	Mg	Si	Sn	C	N	O	H	F
MgF ₂	75	50	350	115	175	400	47	60	1,198	20	300
4 wt-pct MgF ₂ -CaF ₂	100	325	500	145	400	450	61	53	1,150	20	90
12 wt-pct MgF ₂ -CaF ₂	200	>2,600	450	145	400	450	72	73	814	21	110
Reagent-grade CaF ₂	<43	500	243	60	158	<278	108	115	955	22	75
Acid-grade CaF ₂	<63	63	325	48	250	<295	89	63	811	20	140
Native fluor spar (CaF ₂)	<43	438	160	19	420	300	107	119	1,605	28	<50
18.5 wt-pct SrF ₂ -CaF ₂	<50	400	400	50	100	200	110	46	760	21	ND
BaF ₂	<10	100	300	13	90	350	100	134	523	27	50
20 wt-pct LaF ₃ -MgF ₂	<15	50	150	35	95	250	89	61	915	25	150
20 wt-pct LaF ₃ -CaF ₂	50	300	350	40	300	100	105	39	1,792	37	60
4 wt-pct MgF ₂ - 50 wt-pct LaF ₃ -CaF ₂	<100	>5,000	400	135	250	350	125	45	791	18	63
52 wt-pct LaF ₃ -CaF ₂	150	1,300	500	110	300	450	84	69	504	19	125
75 wt-pct LaF ₃ -CaF ₂	100	2,500	225	90	225	200	92	50	870	23	70
LaF ₃	<50	<50	400	45	200	300	123	57	779	27	78
Vacuum arc	<50	<82	525	<19	125	<340	64	113	713	17	ND
Electrode stock	<10	<15	<10	154	103	<154	91	47	685	52	ND

ND = Not determined.

¹ Ni <35; Ca, Cr, V, Y <50; Mn ≤75; Mo <100; Pb <200 ppm on all melted ingots.NOTE.—Values listed are averages of samples taken approximately 2.5 cm from the top and 5.1 cm from the bottom of the same ingot except in CaF₂, LaF₃, and vacuum-arc melts; in these cases the average of 2 melted ingot samples taken as explained above is shown.

Values for electrode stock are averages of 12 determinations on as-received sponge samples for all except C, O, and N, which are averages of samples taken from 10 melted buttons.

Table 15.—*Ingot impurity levels in electroslag-melted titanium as a function of amount and type of added flux-reducing agent*

Flux composition	Impurity, ppm ¹											
	Al	Cu	Fe	Mg	Si	Sn	Y	C	N	O	H	F
1 wt-pct C-CaF ₂	25	15	90	35	70	<100	<50	455	29	1,308	33	93
1 wt-pct C-9 wt-pct MgF ₂ -CaF ₂	<10	550	50	10	<40	<100	<50	562	112	837	30	93
3 wt-pct C-CaF ₂	20	35	100	35	200	100	<50	2,781	41	750	27	90
5 wt-pct C-CaF ₂	30	35	100	15	150	100	<50	2,529	44	1,131	28	70
2 wt-pct Y-CaF ₂	25	10	350	25	100	<100	300	113	44	1,276	26	ND
5 wt-pct Y-CaF ₂	45	10	350	50	250	<100	800	124	50	1,260	30	ND
3 wt-pct Gd-CaF ₂	<25	125	45	30	500	300	<50	97	59	1,528	29	<23

ND = Not determined.

¹ Ca, Cr <10; Ni <20; V <40; Mn ≤50; Mo ≤60; Pb <100 ppm on all melted ingots.

NOTE.—Values listed are averages of samples taken approximately 2.54 cm from the top and 5.08 cm from the bottom of the ingots.

Table 16.—*Ingot impurity levels in electroslag-melted titanium as a function of amount and type of volatile flux addition*

Flux composition	Impurity, ppm ¹										
	Al	Cu	Fe	Mg	Si	Sn	C	N	O	H	F
5 wt-pct CaCl ₂ -CaF ₂	<65	>5,000	400	75	350	350	96	41	909	36	ND
10 wt-pct CaCl ₂ -CaF ₂	<50	5,000	600	70	150	<290	91	40	886	43	ND
20 wt-pct CaCl ₂ -CaF ₂	<50	>5,000	600	50	175	400	90	34	954	45	ND
30 wt-pct CaCl ₂ -CaF ₂	<50	3,000	500	40	<100	<180	96	46	846	63	ND
5 wt-pct K ₂ TiF ₆ -CaF ₂	<10	300	100	5	75	250	76	126	886	27	110

ND = Not determined.

¹ Ni <35; Ca, Cr, V, <50; Mn <75; Mo <100; Pb <200 ppm on all melted ingots.

NOTE.—Values listed are averages of samples taken approximately 2.5 cm from the top and 5.08 cm from the bottom of the ingot.

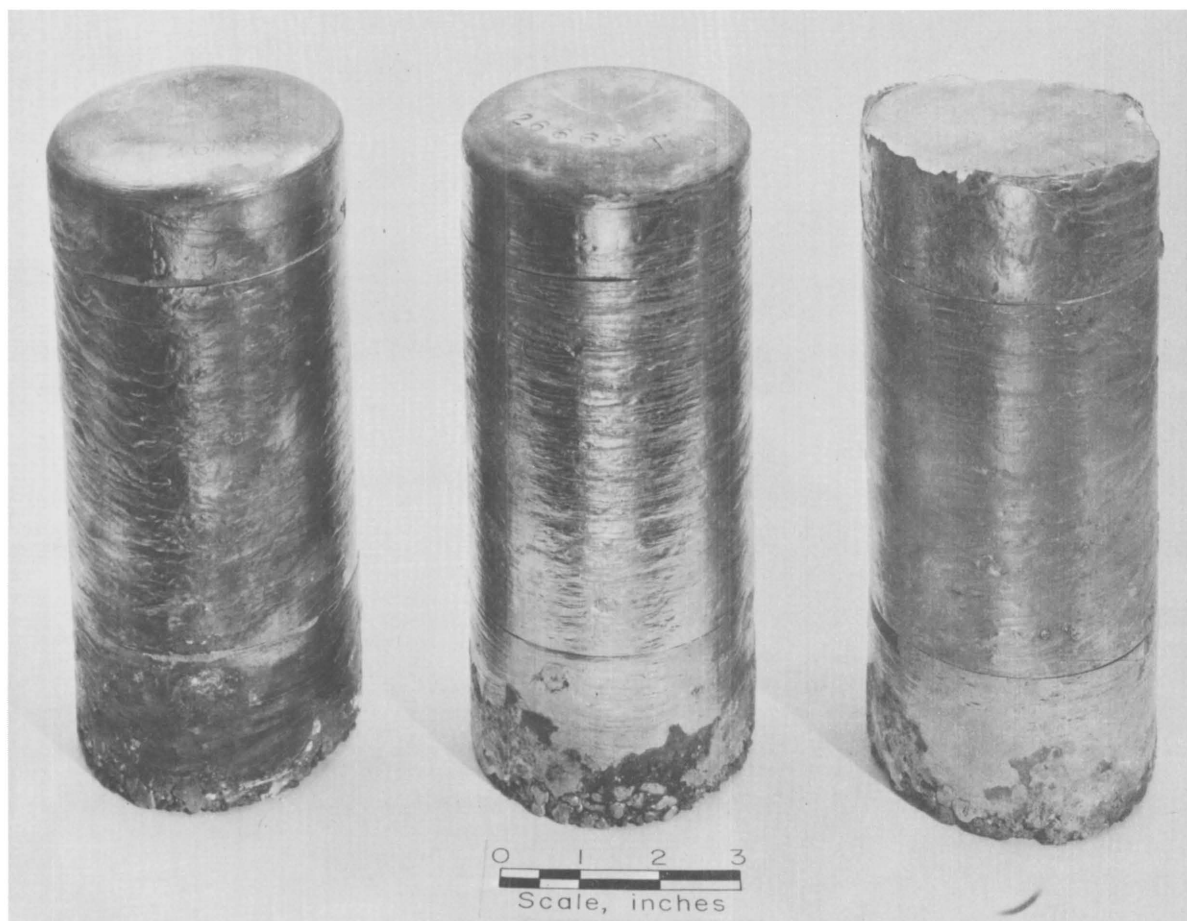


Figure 49.—Titanium ingots electroslag-melted under 1 wt-pct C-CaF₂ fluxes and with (left to right) straight (–) dc electrode polarity and static 1/3 atm of helium, reverse (+) dc electrode polarity and static 1/3 helium atm, and straight polarity and a helium “sweep” atmosphere. Ingots have been cut for sampling.

Microprobe analyses for fluorine on swaged rods showed no fluoride grains present in vacuum-arc-melted material and 1- to 5-micrometer grains well dispersed over the surface of electroslag-melted titanium. No calcium was observed, which indicates that the grains could not be entrapped CaF₂ or calcium fluorotitanates. One alternative is that TiF_n is present, although thermochemistry alone does not predict this. (See chapter 5.) Perhaps other factors are acting to enhance the reactions given in chapter 5, in which case calcium is formed and is subsequently volatilized under the conditions of melting. Alternatively, other reactions to form TiF_n or Ti-O-F are possible.

Effects of Selected Melting Parameters

The composition of the flux is one of several input parameters that may affect the chemical

purity of the resulting ingot. Three additional melting parameters were studied to determine their effect on impurity contents of electroslag-melted titanium ingots, which, in turn, determined to a large extent the mechanical properties and workability of the melted metal. These parameters are—

Furnace atmosphere including—

- Air.
- Static helium at 1/3 atm total pressure.
- Dynamic helium “sweep” at 1/3 atm total pressure.
- Full vacuum.

Consumable electrode power including—

- Straight polarity dc (electrode negative).
- Reverse polarity dc.
- Single-phase ac.

Electrode sponge stock to include—

- Magnesium-reduced, vacuum distilled material.
- Magnesium-reduced, leached and dried titanium.

Table 17.—*Values of D'/D (see text) for important impurities as a function of flux composition in electroslag melting of titanium (all percentages by weight)*

SA run	Ti metal ²	Flux	Impurity ¹					
			Al	C	Fe	Mg	N	Si
25897	VDS	Reagent CaF ₂	(³)	8.67	0.34	0.03	1.21	16.77
26158	LDS	 do	0.11	1.86	2.33	.002	>.93	20.28
26159	LDS	 do	.39	2.85	3.50	.002	>1.62	>15.17
26249	VDS	Reagent CaF ₂ recycled	>.55	.71	>17.67	.12	>1.27	>3.85
26121	VDS	Acid CaF ₂	(³)	10.00	.63	<.02	4.47	41.67
26122	VDS	 do	>.70	2.59	6.14	1.26	<.94	>218.75
26207	LDS	 do	2.09	3.61	.42	<.001	1.24	52.63
26246	VDS	Acid CaF ₂ recycled	(³)	1.26	3.00	<.01	1.51	>4.50
26183	VDS	MgF ₂	>.30	.84	.62	NA	.60	3.42
26185	VDS	4 pct MgF ₂ -CaF ₂	>1.14	.31	2.42	1.57	<.62	4.00
26193	VDS	12 pct MgF ₂ -CaF ₂	>1.52	.29	>10.50	.55	<1.00	58.75
26294	VDS	LaF ₃	(³)	1.81	(³)	.001	.97	(³)
26295	VDS	LaF ₃	(³)	4.08	(³)	>.001	2.34	(³)
26198	VDS	52 pct LaF ₃ -CaF ₂	>3.32	2.64	15.58	.18	>1.86	<1.85
26319	VDS	75 pct LaF ₃ -CaF ₂	>3.24	3.44	.80	.05	.97	(³)

NA = No analysis.

¹ When an impurity analysis is reported as either an upper or lower limit, this results in an inexact value for D' or D and hence either upper or lower limits for D'/D can be given.² VDS = Mg-reduced, vacuum-distilled sponge; LDS = Mg-reduced, leached, and dried sponge.³ Chemical or spectrographic analyses gave only upper or lower limits for impurity, making ratio calculations meaningless.Table 18.—*Ratios of ingot impurity to electrode impurity in electroslag melting of titanium (all percentages by weight)*

SA run	Ti metal	Flux	Impurity ¹							
			Al	C	Fe	H	Mg	N	O	Si
26385	(²)	Reagent CaF ₂	>1.00	0.93	1.06	0.39	0.32	1.08	1.41	1.00
26487	(²)	Acid CaF ₂	>.70	1.44	1.80	.76	.09	.82	4.02	(³)
26488	(²)	 do	>.20	1.04	>.23	.96	<.17	1.90	1.74	<.30
26408	(²)	Acid CaF ₂ recycled	>1.20	.91	1.20	.41	<.20	1.46	1.20	1.00
26340	(²)	5 pct CaCl ₂ -CaF ₂	(³)	1.00	1.07	.67	.30	1.11	1.28	2.33
26364	(²)	7.5 pct CaCl ₂ -CaF ₂	.88	1.12	1.29	.96	.02	1.04	1.26	1.33
26343	(²)	10 pct CaCl ₂ -CaF ₂	(³)	.91	1.60	.80	.28	1.08	1.25	1.50
26344	(²)	20 pct CaCl ₂ -CaF ₂	(³)	.92	1.60	.83	.20	.92	1.35	1.75
26384	(²)	23 pct CaCl ₂ -CaF ₂	2.22	.78	1.18	.97	.03	1.03	1.40	2.00
26347	(²)	30 pct CaCl ₂ -CaF ₂	(³)	1.00	1.33	1.17	.16	1.24	1.19	<1.00

¹ An impurity analysis reported as either an upper or lower limit results in an inexact value for the ratio shown in this table, and these are therefore given as appropriate upper and lower limits.² Mg-reduced, vacuum-distilled sponge.³ Mg-reduced, gas-swept and/or water-leached sponge.⁴ Na-reduced, leached and dried sponge.⁵ Mg-reduced, leached and dried sponge.⁶ Spectrographic analysis gives only upper and lower limit for electrode and ingot, and hence ratio cannot be calculated.

The effect of the aforementioned parameters on ingot impurity levels is illustrated in the data presented in tables 20 through 22. The following conclusions may be drawn from these data:

1. Electrode stock is the most significant parameter among those studied for determining ingot impurity levels during electroslag melting of titanium. Except for carbon, most impurities are lower when vacuum-distilled sponge is used.

Electrode stock has little systematic effect on ingot copper, fluorine, and oxygen.

2. A dynamic helium furnace atmosphere and reverse consumable electrode polarity do not improve ingot purity, except for magnesium in the case of the dynamic furnace atmosphere. This is due to the greater relative volatility of this impurity under conditions of interest.

3. Electroslag melting with reagent-grade CaF_2 results in ingots with greater hydrogen, fluorine, and magnesium compared with vacuum-arc-melted material.

4. Copper, oxygen, nitrogen, and fluorine are at a maximum when titanium is air-melted with flux, and oxygen levels are minimized in ingots melted under a static $\frac{1}{3}$ atm of helium. Ingot

magnesium, nitrogen, and copper are minimized when a full vacuum is used.

5. Reverse dc polarity decreased ingot oxygen, and ingots melted with ac show minimum magnesium and nitrogen.

No significant correlation can be made of ingot hardness as a function of flux composition or melting parameters with the exception of car-

Table 19.—Average ingot fluorine analyses for electroslag-melted titanium (all percentages by weight)

SA run	Ti metal ¹	Flux	dc polarity	Furnace atmosphere	F, ppm
25897	VDS	Reagent CaF_2	Straight	Static He at $\frac{1}{3}$ atm	85
26158	LDS	do	do	do	120
26159	LDS	do	do	do	125
26121	VDS	Acid CaF_2	do	do	130
26122	VDS	do	do	do	150
26207	LDS	do	do	do	85
26514	LDS	CaF_2	Reverse	Dynamic flowing He at $\frac{1}{3}$ atm	50
26515	LDS	CaF_2	do	Static He at $\frac{1}{3}$ atm	55
26516	LDS	CaF_2	Straight	Dynamic full vacuum	110
25617	VDS	CaF_2	do	do	95
26183	VDS	MgF_2	do	Static He at $\frac{1}{3}$ atm	300
26185	VDS	4 pct MgF_2 - CaF_2	do	do	90
26193	VDS	12 pct MgF_2 - CaF_2	do	do	110
26294	VDS	LaF_3	do	do	85
26295	VDS	LaF_3	do	do	70
26198	VDS	52 pct LaF_3 - CaF_2	do	do	125
26319	VDS	75 pct LaF_3 - CaF_2	do	do	70

¹ VDS = Mg-reduced vacuum-distilled sponge; LDS = Mg-reduced leached and dried sponge.

Table 20.—Effect of furnace atmosphere on impurities in electroslag-melted titanium

Atmosphere	Impurities ppm ¹										
	Al	Cu	Fe	Mg	Si	Sn	C	N	O	H	F
Air	<50	937	300	45	<175	<210	134	1,730	2,244	22	105
Static $\frac{1}{3}$ atm helium	<63	63	325	48	250	<295	89	63	811	20	75
Helium "sweep"	<20	650	290	25	240	400	100	123	1,506	27	90
Full vacuum	25	10	300	<5	250	150	123	35	1,616	25	95

¹ Ca, Cr, Ni, V, Y <50; Mn <60; Mo ≤110; Pb <200 ppm in all ingots.

NOTE.—Values listed are averages of samples taken approximately 2.5 cm from the top and 5.08 cm from the bottom of the ingot. All ingots were melted with magnesium-reduced, vacuum-distilled sponge, straight dc polarity (electrode negative), and CaF_2 flux.

Table 21.—Effect of consumable electrode current on impurities in electroslag-melted titanium

Current	Impurity ppm ¹										
	Al	Cu	Fe	Mg	Si	Sn	C	N	O	H	F
Straight polarity dc	<43	500	243	60	158	<278	108	115	955	22	75
Reverse polarity dc	<50	≤50	500	50	125	250	101	96	720	26	120
Alternating current	<50	≤50	475	28	100	<265	96	53	1,036	25	90

¹ Ni <35; Ca, Cr, Mn, Mo, V <50; Pb <200 ppm in all ingots.

NOTE.—Values listed are averages of samples taken approximately 2.5 cm from the top and 5.08 cm from the bottom of the ingot. All ingots melted with magnesium-reduced, vacuum-distilled sponge, under a static $\frac{1}{3}$ atm of helium, and CaF_2 flux.

Table 22.—Effect of electrode sponge stock on impurities in electroslog-melted titanium

Sponge stock	Ingot impurity, except as indicated, ppm ¹										
	Al	Cu	Fe	Mg	Si	Sn	C	N	O	H	F
VACUUM-ARC MELT, NO FLUX, STRAIGHT POLARITY											
Vacuum-distilled	<50	<82	525	<19	125	<340	64	113	713	17	ND
Leached and dried ..	488	<50	425	<19	213	<180	70	138	531	46	ND
FULL VACUUM, STRAIGHT POLARITY, ACID-GRADE CaF ₂ FLUX											
Vacuum-distilled	25	10	300	<5	250	150	123	35	1,616	25	95
Leached and dried ..	500	<10	650	10	300	<100	68	111	867	153	110
HE SWEEP, REVERSE POLARITY, REAGENT-GRADE CaF ₂ FLUX											
Vacuum-distilled	<50	<50	600	40	100	250	94	62	643	25	105
Leached and dried ..	600	<15	800	135	350	<100	70	126	1,463	197	35
STATIC 1/3 HE ATM, STRAIGHT POLARITY, REAGENT-GRADE CaF ₂ FLUX											
Vacuum-distilled	<43	500	243	60	158	<278	108	115	955	22	75
Leached and dried ..	200	<50	500	110	700	<180	47	113	1,052	146	85
ELECTRODE IMPURITY (PPM)											
Vacuum-distilled	<10	<15	<10	154	103	<154	91	47	685	52	ND
Leached and dried ..	660	<10	<336	>5,000	286	<180	69	117	655	219	ND

ND = Not determined.

NOTE.—Values for electrode stock are averages of 12 determinations on as-received sponge samples for all except C, O, and N, which are averages of samples taken from 10 melted buttons. In all cases, Ni <35; Ca, Cr, Mn, Mo, V <50; Pb <200 ppm.

NOTE.—Values listed are averages of samples taken approximately 2.5 cm from the top and 5.1 cm from the bottom of the same ingot except in CaF₂, LaF₃, and vacuum-arc melts; in these cases the average of 2 melted ingot samples taken as explained above is shown.

bon flux additions. Metal melted under CaF₂ fluxes ranges from 144 to 179 on the Brinell scale. As expected in the case of carbon slag additions, average Brinell hardness is higher (172–204) as measured with a 10-mm steel ball under a 3,000-kg load.

Flux bath temperatures during melting, as measured with a two-color ratio pyrometer, also show a lack of correlation with the aforementioned melting parameters with the same exception. Temperatures of 1,680° C ± 40° were usually obtained except when carbon was added to the flux, in which case measured temperatures were 1,850° C ± 40°. This may have been an emissivity effect due to carbon particles.

The inability of appropriate fluxes to remove impurities is probably largely related to the insolubility of such impurities in the highly ionizing fluorides relative to the reactive molten metals under conditions of interest. Changes in electrical parameters and furnace atmospheres are also unable to overcome such impurity affinity of the metal. Resulting ingot quality is believed to be related to the physical and chemical properties of the slag or to other melting parameters. Refinements of reactive metals

during melting are much less dependent on the slag than in the case of electroslog refining of iron and steels.

Ingot Microstructure

Electrode polarity and furnace atmosphere exert essentially no effect on the microstructure of electroslog-melted titanium ingots. Melting of vacuum-distilled sponge results in ingots with fewer inclusions than those melted from magnesium-reduced, leached and dried sponge. Larger grain size is evident in metal melted under acid-grade CaF₂ compared with that from reagent-grade CaF₂ melts. Fewer inclusions are present in metal melted under fluxes with LaF₃ and carbon additions, whereas CaCl₂ and MgF₂ flux additions result in metal with more inclusions, as shown in the photomicrographs in figure 50. Inclusions are thus related to high-temperature flux stability. For comparison, metal melted with reagent-grade CaF₂ is also illustrated (fig. 51).

In figures 50 and 51, the dark large and small areas are voids and pits, whereas the small grains which often are present in chains are believed to be inclusions in the titanium. The metal melted with LaF₃ and 30 weight-percent CaCl₂–CaF₂ shows an austenitic texture which may be

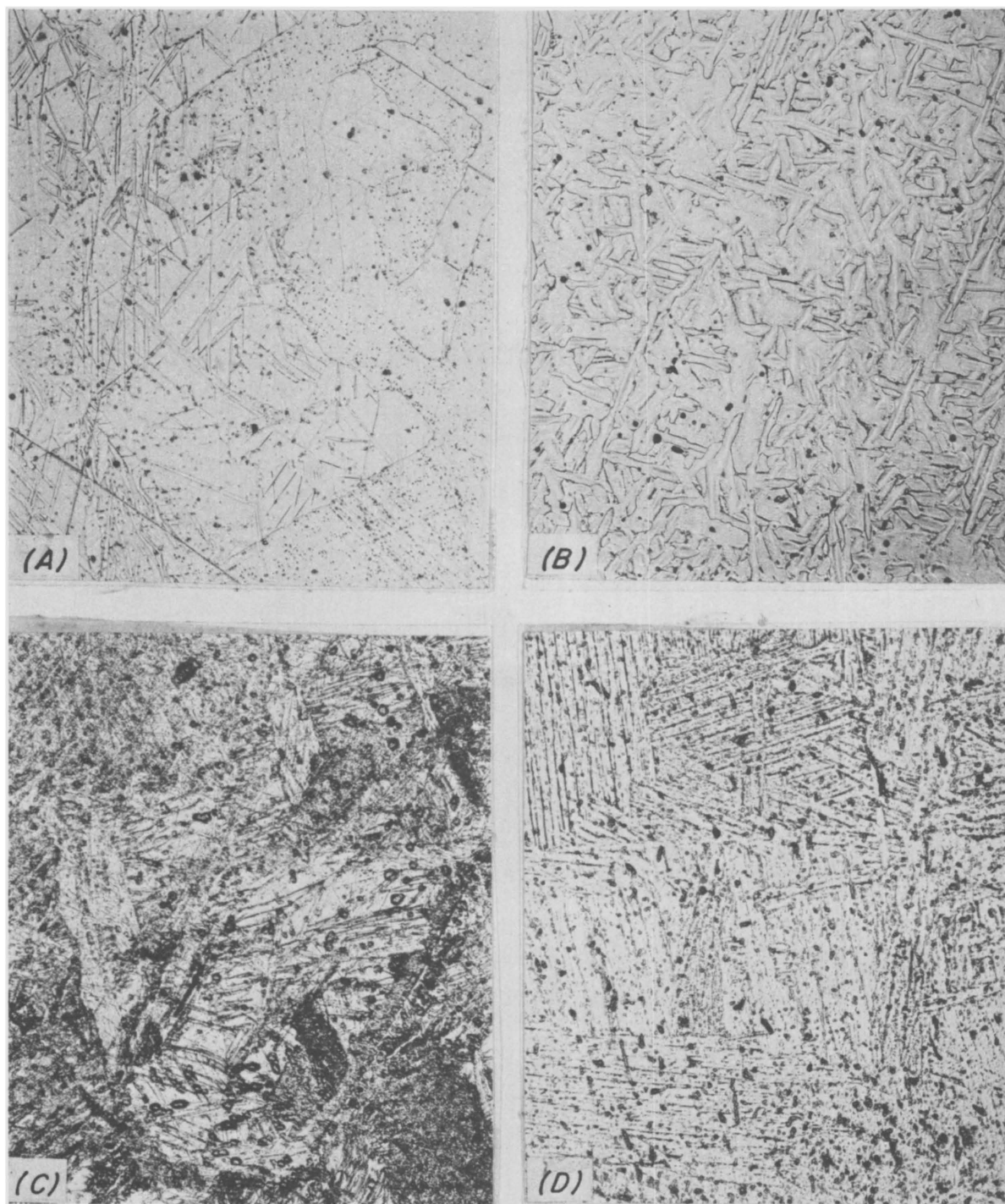


Figure 50.—Photomicrographs ($\times 100$) of single-electroslag-melted titanium ingots from vacuum-distilled sponge, using four slag compositions: *A*, LaF_3 , *B*, 3 wt-pct C- CaF_2 , *C*, 30 wt-pct CaCl_2 - CaF_2 , and *D*, MgF_2 . Surfaces have been etched with $\text{HF-HNO}_3\text{-H}_2\text{O}$. Straight polarity dc and $\frac{1}{3}$ atm helium used in all cases.

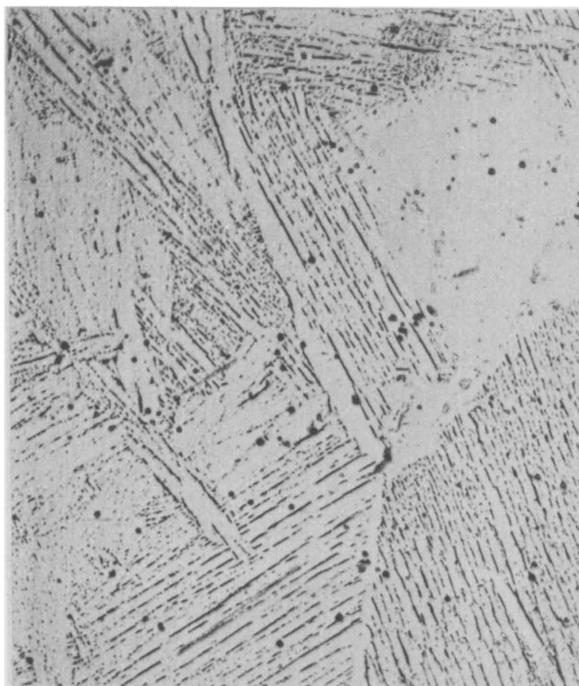


Figure 51.—Photomicrograph ($\times 100$) of single-electroslag-melted titanium ingot from vacuum-distilled sponge using reagent-grade CaF_2 . Surface etched with $\text{HF-HNO}_3\text{-H}_2\text{O}$; straight polarity dc and $\frac{1}{3}$ atm helium.

due to a transformation as a result of heat generated when the sample was cut. The grains are well defined in figures 50B and 51 but are somewhat jagged in the other photomicrographs. Grain size can also be noted in figures 50A, 50B, and 51. No noticeable grain boundary inclusions are evident in any of the photomicrographs shown. The metal melted with carbon flux additions (fig. 50B) shows small fragments and a more uniform grain structure. Metal melted with MgF_2 and CaF_2 shows variable grain orientation, with the grains often intersecting at 120° , as well as segregated grain imperfections. Grain boundaries are clearly delineated in figures 50A, 50B, and 51.

ELECTROSLAG MELTING OF TITANIUM ALLOYS

Data have been accumulated on titanium alloy homogeneity as a result of electroslag melting. Two 10-cm-diameter ingots of two alloys—titanium-6 percent aluminum-4 percent vanadium, and titanium-8 percent manganese—were examined for retention of alloying constituents and segregation. One electrode of each alloy was

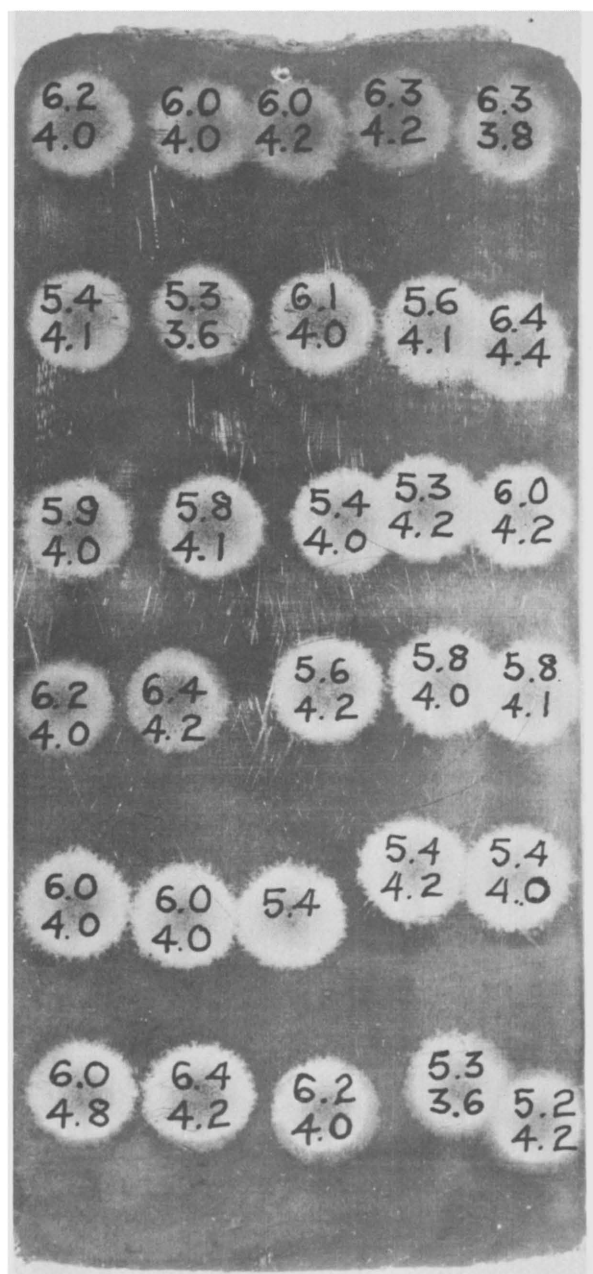


Figure 52.—Percentage distribution of aluminum (top values) and vanadium (bottom values), Ingot SA 25928.

forged alloy bar stock, and the other electrodes were pressed sponge containing the alloying addition as small pieces of aluminum, vanadium, or manganese. The ingots were melted in $\frac{1}{3}$ atm of helium. The flux was purified calcium fluoride. Melting was accomplished with 4,500 amperes and 20 to 22 volts. The melting rate was approxi-

mately 0.45 kg min⁻¹. About 3 kilowatts per kilogram of metal was required. Ingot SA 25887—a titanium-6 percent aluminum-5 percent vanadium alloy melted from forged bar stock—was analyzed for aluminum content by the atomic absorption method, for vanadium content by a wet chemical method, and for both aluminum and vanadium content by direct-reading spectrographic analysis. Nine samples were machined from the ingot: one at the surface, one just below the surface, and seven at different locations within the ingot. The ingot was sparked in 25 locations for spectrographic analysis. The results are shown in table 23. Analyses of the electrode for this melt averaged 6.43 percent aluminum and 4.00 percent vanadium. Considering the accuracy of the analytical methods, the average values of aluminum and vanadium for both electrode and ingot indicate the retention of the alloy constituents to be excellent.

Table 23.—Analyses obtained for ingot SA 25887, Ti-6Al-4V alloy electroslag melted from forged bar stock

Aluminum, percent		Vanadium, percent	
Atomic Absorption	Spectrographic	Wet Chemistry	Spectrographic
¹ 6.20	6.1	¹ 3.91	3.8
² 6.25	6.4	² 3.89	4.0
6.79	6.6	3.88	4.1
5.92	6.3	3.80	3.9
6.25	6.4	3.84	3.6
6.38	6.4	3.84	4.1
6.63	6.4	3.80	4.0
6.40	6.3	3.86	3.8
6.63	6.3	3.90	3.8
6.38 (av)	6.7	3.86 (av)	3.9
	6.4		4.2
	6.2		3.6
	6.5		3.7
	6.3		4.0
	7.2		4.2
	6.4		4.1
	6.2		3.8
	6.0		3.6
	6.5		3.6
	6.8		4.1
	6.0		3.5
	6.1		3.8
	5.9		3.8
	5.9		3.8
	6.4		4.0
	6.35 (av)		3.87 (av)

¹ Sample from surface of ingot.

² Sample from immediately beneath surface of ingot.

NOTE.—Accuracy for both the atomic absorption and wet chemistry methods is ± 3 percent of the amount present. Accuracy for the direct-reading spectrographic method is ± 5 percent of the amount present.

Furthermore, little alloy segregation is evident. An impurity analysis made for this ingot revealed a slight increase in the concentrations of iron, manganese, and silicon from top to bottom of the ingot.

Ingot SA 25928—a titanium-6 percent aluminum-4 percent vanadium alloy—was prepared by electroslag melting a pressed sponge electrode containing small pieces of aluminum and vanadium uniformly distributed throughout the electrode. The ingot was analyzed by the direct-reading spectrographic method to obtain the results shown in figure 52. The average values were 5.84 percent aluminum and 4.08 percent vanadium, indicating no significant loss of the alloying additions. Within the accuracy of the analytical methods, the ingot was homogeneous.

Two titanium-manganese alloy ingots—SA 25923, melted from a forged bar electrode containing 7.5 percent manganese, and SA 25932, melted from pressed sponge containing pieces of manganese totaling 8 percent—were also analyzed by the direct-reading spectrographic method. The results are shown in figures 53 and 54. For both ingots, it appears that some manganese was lost during melting. The average manganese contents were 6.05 percent for ingot SA 25923 and 7.00 percent for ingot SA 25932. In both ingots, but especially in SA 25932, which was the ingot melted from a sponge electrode, the manganese content is higher near the surfaces of the ingot. The macrostructure of ingot SA 25932 revealed banding, which has been attributed to manganese segregation in arc-melted ingots. The macrostructure of this ingot is shown in figure 55. Improved melting techniques or improved methods of adding the manganese appear necessary before homogeneous ingots of the titanium-8 percent manganese alloy can be prepared by the electroslag melting process.

ELECTROSLAG MELTING OF ALUMINUM AND ITS ALLOYS

When considering the electroslag process as it applies to light metals such as titanium, mention should be made of limited literature results of electroslag melting aluminum and its alloys.

The only reported electroslag scheme for melting pure or unalloyed aluminum consists of introducing the molten metal from a holding furnace into a molten flux consisting of 23 percent cryolite (Na_3AlF_6), 47 percent NaCl, and 30 percent KCl. A current of 275 amperes at 5 to 6 volts dc was employed. The molten, re-

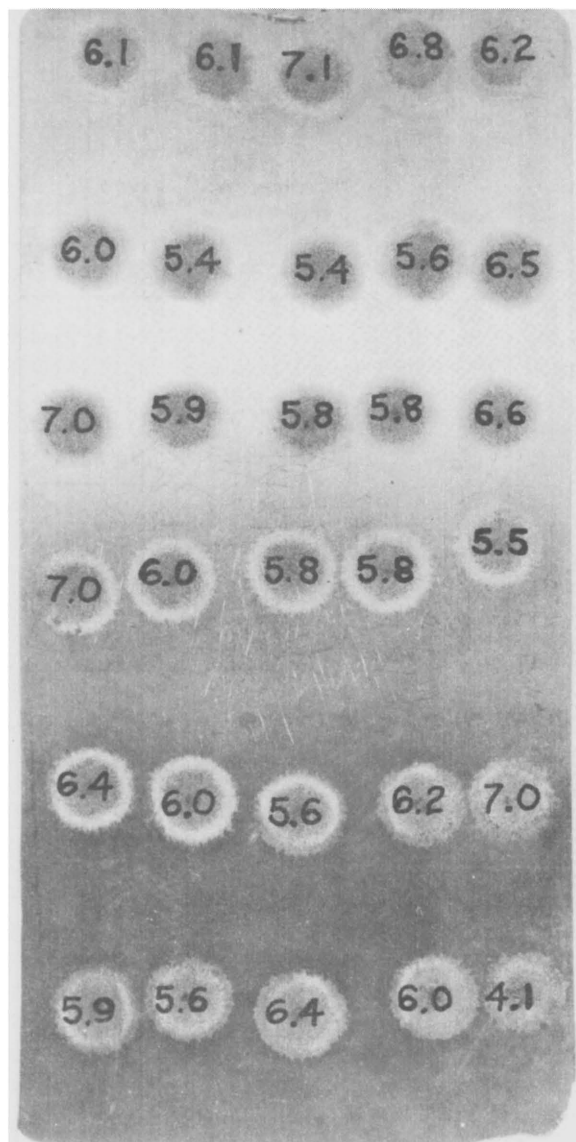


Figure 53.—Percentage distribution of manganese, Ingot SA 25923.

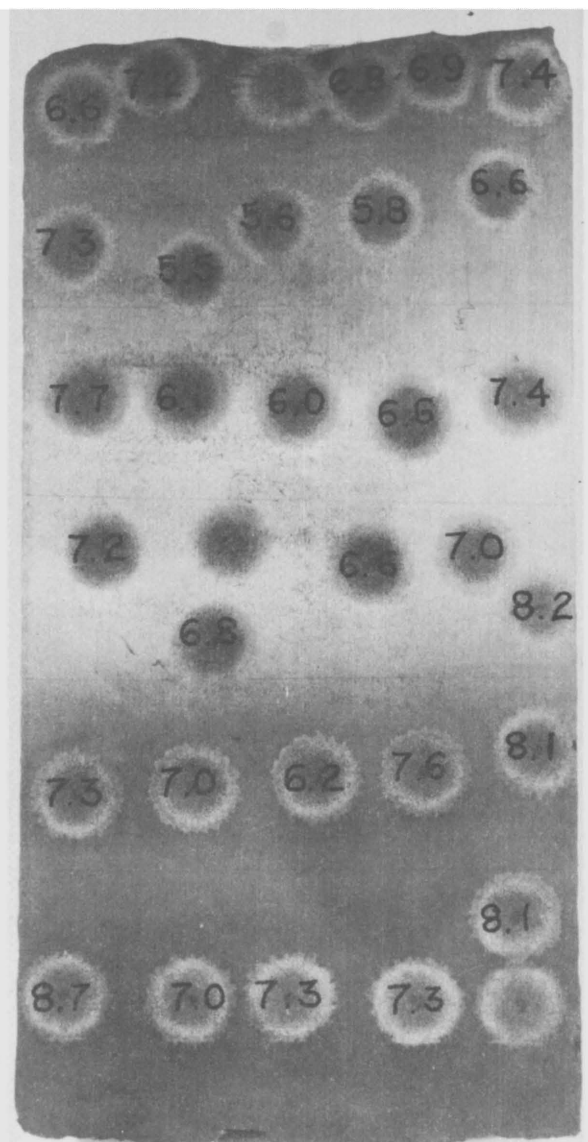


Figure 54.—Percentage distribution of manganese, Ingot SA 25932.

finer metal solidified to form 370 to 540-mm-diameter ingots (1).

Several reports on electroslag melting aluminum alloys have been published. For aluminum-magnesium alloys, the aforementioned scheme uses carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$). Variations involving the heat source of the flux, for example, ac graphite electrodes (7) and steel rings (1), and the flux (chlorides and fluorides) have also been described. Reduction

of hydrogen and microporosity in electroslag-melted aluminum alloys was accomplished using molten $90\text{KCl} \cdot \text{MgCl}_2 \cdot 10\text{MgF}_2$ and $47\text{KCl} \cdot 30\text{NaCl} \cdot 23\text{Na}_3\text{AlF}_6$ fluxes (4). Wilson, Hough, and Goble (11) have reported dc electroslag melting of Al-2.5 Mg alloys as a means for inclusion removal. Two problems identified were (1) the requirements of relatively high current densities to maintain uniform melting due to high heat losses, and (2) too rapid cooling of

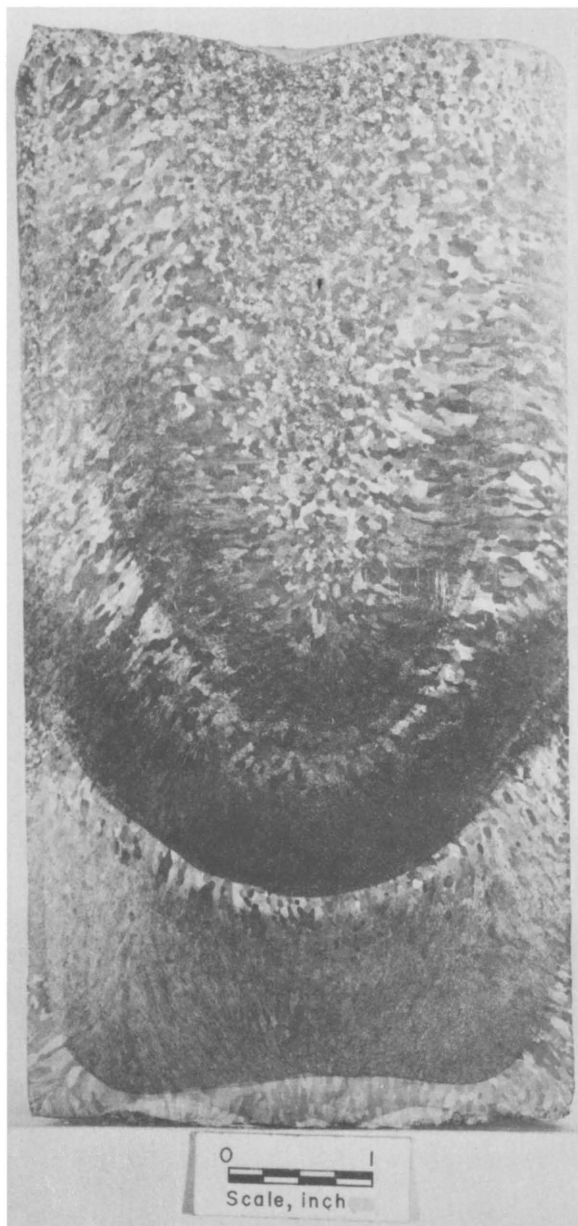


Figure 55.—Titanium-manganese alloy ingot section.

the crucible by flowing water. Fluxes used were alkali fluoride- AlF_3 compositions or a ternary Li, Na, K-cryolite composition. At least 80 percent of the original inclusions were satisfactorily removed. However, poor sidewalls and high magnesium losses (up to 85 percent using dc positive polarity) limited the utility of electroslag melting aluminum alloys.

Ishchenko, Lychko, and Omel'chenko (8) described a technique whereby an aluminum alloy is melted under a 30 percent $\text{NaF-KCl-Na}_3\text{AlF}_6$ flux (the latter two components can range from 10 to 40 percent) and subsequently teemed into a steel mold. Then an additional aluminum alloy electrode is melted under the flux blanket into the top of the ingot. This fills the shrinkage cavity and promotes axial solidification due to the generation of heat at the ingot top.

A published note (2) describes work at the E. O. Paton Electric Welding Institute in Kiev in which droplets of aluminum bronze and aluminum-base magnesium alloys pass through a chloride-fluoride flux. Low ac voltage graphite electrodes maintain a molten flux.

CONCLUSIONS

As a result of favorable Soviet reports on electroslag melting titanium, the Bureau of Mines undertook to verify the U.S.S.R. claims and evaluate the process. Of the several hoped-for advantages, only the controlled melt rate and improved sidewall can be considered as realized.

The quality of electroslag-melted ingots of titanium is mainly dependent on the quality of the electrode sponge material. The electroslag melting process does not remove hydrogen from the metal. If high-hydrogen sponge is used, the material must be vacuum-arc-melted first. Pre-fused, acid- or reagent-grade calcium fluoride is the ultimate flux of choice. Flux remaining in the crucible on top of the ingot at the end of a melt can be reused without further treatment. Ingots with smooth sidewalls suitable for forging without surface conditioning can be produced under optimum melting conditions. Furnace atmosphere and consumable electrode polarity exert minimal effect on the ingot purity. Ingot inclusion content is related to high-temperature flux stability.

Two titanium alloys (Ti-6Al-4V and Ti-8Mn) were electroslag-melted. Retention of the alloying constituents except manganese was judged to be excellent. Segregation of aluminum and vanadium was minimal.

Electroslag melting of aluminum alloys produces satisfactory ingots only when careful attention is paid to the narrow choice of fluxes and operating parameters.

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* Titles enclosed in parentheses are translations from the language in which the item was published.

CHAPTER 8.—LARGE-SCALE ELECTROSLAG MELTING OF TITANIUM ¹

By R. A. Beall ² and P. G. Clites ³

One purpose of this research was to produce slab-shaped ingots of sufficient size to establish the suitability of electroslag melting for the production of ingots on an industrial scale. A comparative evaluation was to be made of slab-shaped ingots produced by electroslag melting titanium sponge from different sources and of slab-shaped ingots produced by vacuum-arc melting. A furnace, capable of both vacuum-arc and electroslag melting, was built for producing slab-shaped ingots with 17.8 by 50.8-cm (7- by 20-inch) cross section. These dimensions for the ingot cross section were an arbitrary compromise between the large scale desired to verify the adaptability of the process to industrial scale and the limitation imposed by the available power supply for melting. Provisions were also made for melting ingots with a circular cross section as large as 30.5 cm (12 inches) in diameter.

THE FURNACE

Figure 56 is a cross section of the furnace. The furnace chamber was constructed of three mild-steel tubular sections. The lower section, which houses the crucible, was 76.2 cm (30 inches) in diameter and 152.4 cm (60 inches) long. The middle section was also 152.4 cm long but only 61 cm (24 inches) in diameter and was equipped with access doors. Both the middle and the lower sections were mounted on a trolley and could be rolled forward from under the furnace platform for loading and unloading the furnace. The short (35.6 cm, or 14 inches long) upper section of the furnace was mounted directly to the platform. This platform also supported a tripod which carried the electrode drive and alinement mechanism.

¹ Adapted from Proc. 1st Internat. Symp. on Electroslag Consumable Electrode Remelting and Casting Technology, Pittsburgh, Pa., 1967, Pt. 1; Topical Report to U.S. Army Materials and Mechanics Research Center, Watertown, Mass., USBM-RC-1351, 1969.

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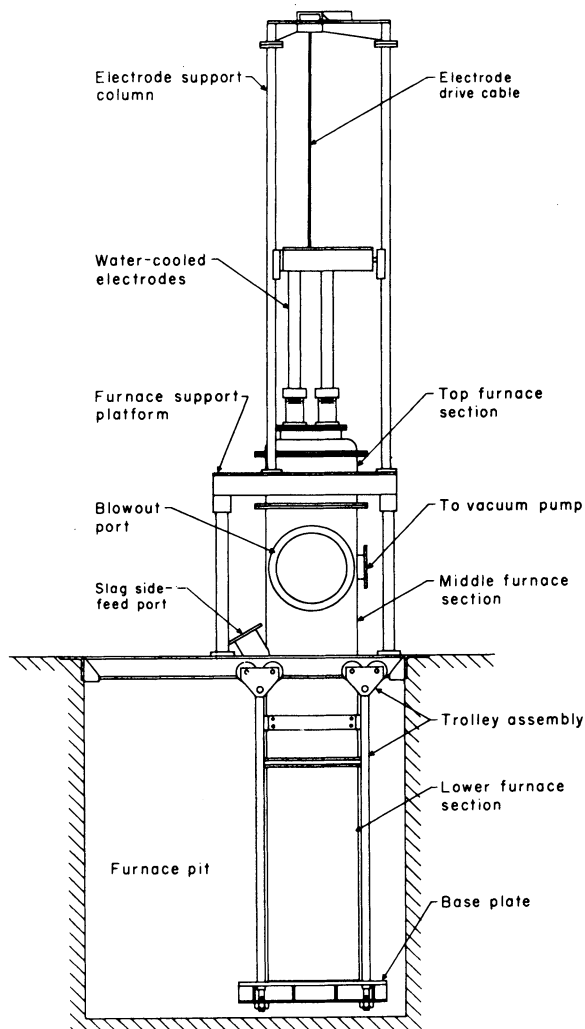


Figure 56.—Prototype furnace for electroslag melting titanium.

Not shown in figure 56 at the front of the furnace is an auxiliary tank for sidefeeding

granular slag during melting. The lower portion of the furnace was below floor level to provide the required headroom. The furnace was equipped with an optical system for remote viewing during melting.

The vacuum system, which was connected to the rear side of the middle furnace section, consisted of a $169.8\text{-m}^3\text{ hr}^{-1}$ (100-cfm) mechanical pump for roughing the chamber and a $2,124\text{-m}^3\text{ hr}^{-1}$ (1,250-cfm) blower backed by a $237.8\text{-m}^3\text{ hr}^{-1}$ (140-cfm) mechanical pump for attaining the ultimate vacuum. This system provided an ultimate vacuum of less than 10 microns.

The copper crucible for producing the slag-shaped ingots is shown in figure 57. This crucible was divided into four sections: two flat sections, each 35.6 cm (14 inches) wide, for the sides, and two curved end pieces. The corners of the end

pieces were curved to a 3.8-cm ($1\frac{1}{2}$ inch) radius on the inside surface. Each of these four sections and the water-cooled copper bottom for the crucible had its own water-cooling circuit. As can be seen in figure 57, inlet and outlet water lines were provided for each section through the bottom plate of the furnace chamber. The crucible sections were bolted together with a simple, metal-to-metal joint; no bolted vacuum-tight joints were required other than those on the water supply lines because the entire assembly was contained in a cylindrical vessel. The crucible section shown in figure 57 was 76.2 cm (30 inches) long. Provisions were made to bolt similar sections to the top of the sections shown for making longer ingots.

Figure 58 shows the water jacket and crucible assembly used to produce round ingots in the



Figure 57.—Crucible for slab-shaped ingots.

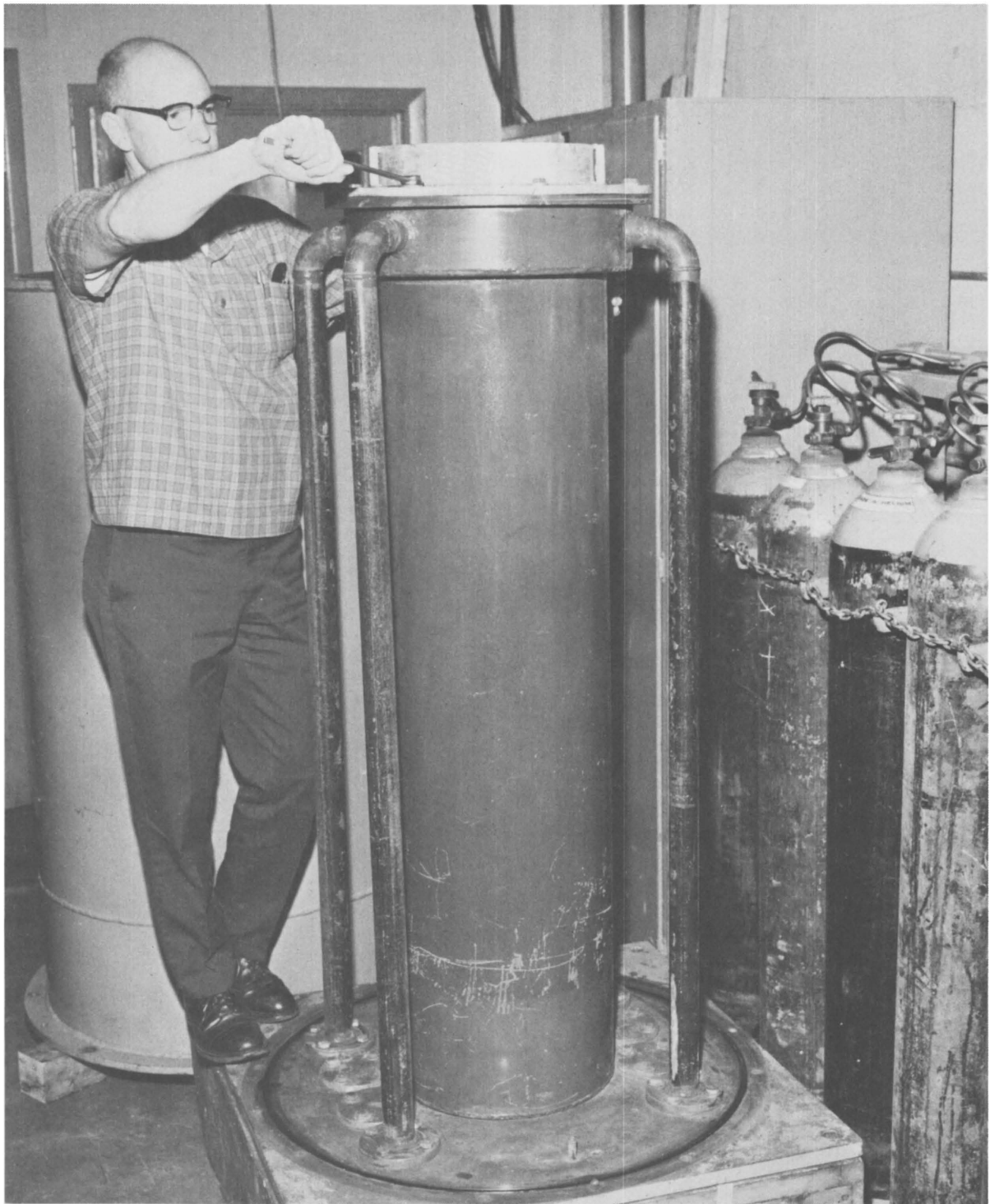


Figure 58.—Crucible and water-jacket assembly for producing 30.5-cm (12-inch) diameter round ingots

prototype furnace. This assembly can be used to product ingots 30.5 cm (12 inches) in diameter and 121.9 cm (48 inches) long.

MELTING PROCEDURES

The prototype furnace was used in a comparative evaluation of slab-shaped ingots prepared by electroslag melting from domestic leached-and-dried sponge, vacuum-distilled sponge, and domestic sponge prepared by a proprietary, gas-swept method. A slab-shaped ingot was also prepared from leached-and-dried sponge by vacuum-arc melting. Melting procedure for vacuum-arc melting did not differ from vacuum-arc melting in any other furnace except for use of the slab-shaped crucible. Electroslag-melting procedures as used with the prototype furnace are similar to those described in chapter 7 and are outlined in the following paragraphs.

For electroslag melting, titanium-sponge electrodes were single-melted to produce an ingot. These electrodes were formed by heliarc welding 5- by 5- by 25.4-cm compacts of sponge into a

slab-shaped electrode with a 10.2- by 40.6-cm cross section. A partially consumed electrode is shown in figure 59.

A pin, usually a 7.6- to 10.2-cm length of 5- by 5-cm sponge bar machined to a point at the end, was welded to the bottom of the electrode to serve as a starting pin. When the electrode was loaded into the furnace, it was lowered until this pin rested on a starting pad placed in the bottom of the crucible. The starting pad was a 1.9-cm-thick section from a previously melted slab-shaped ingot or a 1.9-cm-thick pad of sponge-metal compacts welded together to cover the bottom of the crucible.

After the electrode was lowered onto the starting pad, the entire charge of calcium fluoride flux needed for melting the ingot was loaded into the crucible. The calcium fluoride was treated prior to charging the furnace by the methods outlined in chapter 7. The furnace was evacuated to the ultimate vacuum of the system and then back-filled to approximately $\frac{1}{3}$ atm with helium.

Melting was started by first operating for 3 to



Figure 59.—Partially consumed electrode.

5 minutes with the electrode dead-short to the starting pad. The power was held to a low value of 3,000 to 4,000 amperes and 2 to 3 volts. The electrode was then raised off the starting pad, and the power was maintained at a value at which the calcium fluoride melted but the electrode did not. As soon as the entire charge of calcium fluoride was molten, the power was increased until the electrode melted at a satisfactory rate.

RESULTS

A primary objective of research with this furnace was to determine whether satisfactory slab-shaped ingots could be produced by single melting domestic leached-and-dried titanium sponge. Leached sponge prepared by both sodium reduction and magnesium reduction was tested. Vacuum-distilled sponge from a foreign source and sponge prepared by a proprietary, gas-swept process were also tested.

Procedures developed for the production of small-scale ingots by a single electroslag melting step were described in chapter 7. These small-scale studies showed that the hydrogen content of the sponge was not reduced during electroslag melting; for this reason, leached-and-dried sponge was not considered a satisfactory starting material for producing ingots by electroslag melting. Melting studies with the prototype furnace would not be expected to produce any different results as far as hydrogen content of the metal was concerned. Large-scale tests were conducted, however, to see if large, slab-shaped ingots could be prepared and if these ingots would be suitable for fabrication without surface conditioning.

Variables Noted

During melting studies in the prototype furnace, variables studied included sponge composition, flux depth, electrical parameters, and electrode geometry. In addition, ingots were prepared in the slab-shaped crucible by both conventional vacuum-arc melting and electroslag melting, and ingots were prepared by electroslag melting in the 30.5-cm-diameter round crucible. Alloy ingots were prepared in the slab-shaped crucible from electrodes of previously melted bar stock.

In electroslag melting, approximately 18 to 23 kg of calcium fluoride flux was used for each ingot melted in the 17.8- by 50.8-cm crucible. This provided a minimum flux cover 6.35 to 7.6 cm deep. As the entire charge of flux was added to the crucible prior to the start of melting, the

depth of the flux varied slightly as the melt progressed. The depletion of flux cover during any given melt was related to the quality of ingot wall obtained; if a very rough wall was produced larger amounts of flux were entrapped along the sidewall than if a fairly smooth wall was obtained. No significant difference was noted in the quality of ingot wall from bottom to top of the slab-shaped ingots as a result of decreasing flux depth. However, in several runs when the flux depth decreased much below 5 cm, the voltage drop through the flux cover decreased to a value below that required for satisfactory melting and thus affected sidewall quality.

Table 24 gives pertinent data obtained during melting of ingots in the prototype furnace. It should be noted that total kilowatt-hours, kilowatt-hours per kilogram, and melting rate are all influenced by total ingot weight. During electroslag melting in the prototype furnace, a certain amount of time was involved in melting the initial charge of flux. Consequently, during melting by this method, the overall efficiency of the operation was less for shorter ingots of a given crucible size.

In general, the electroslag melting process was less efficient than arc melting; melting rates were lower and power requirements were higher for electroslag melting. When one considers the fact that electroslag melting yields a finished ingot in one melting operation, the electrical efficiencies of the two processes were more comparable, but vacuum-arc melting was still more efficient. The vacuum-arc-melted ingots required approximately 1.87 kwhr kg^{-1} for double-melted ingot, and the electroslag-melted ingots required from 1.87 to 4.75 kwhr kg^{-1} .

Ingots

The electroslag-melting process as applied to the prototype furnace was unsuccessful to the extent that the process did not yield slab-shaped ingots suitable for direct conversion to sheet or plate. Some machining of the outer surface would be required. The electroslag ingots were, in most cases, sound internally and were superior in this respect to vacuum-arc-melted ingots prepared in the slab-shaped crucible. Considerable subsurface porosity was noted near the sidewalls of the arc-melted ingots. However, no attempt was made to improve operating parameters for arc melting, and it is not known if better arc-melted ingots could be prepared if melting conditions were more carefully established. This same reservation should also apply to electroslag melting,

Table 24.—Data obtained during melting of ingots in prototype furnace

SA run	Electrode composition	Electrode cross section, cm	Melting technique ¹	Ingot weight, kg	Total kwhr	Kwhr kg ⁻¹	Melting rate, kg/min	Nominal melting current, amp	Nominal arc potential, volts
25824	Leached and dried magnesium reduced titanium sponge.	10.2 x 40.6	Vacuum-arc first melt	233	216	0.92	4.49	9,000–9,500	29–30
25877	Remelt SA 25824.	8.3 x 30.5	Vacuum-arc remelt	210	195	.92	4.91	9,300	32–33
25835	Leached and dried magnesium reduced titanium sponge.	10.2 x 40.6	Electroslag	240	453	1.89	3.54	10,500–12,000	30
25886	Vacuum distilled magnesium-reduced titanium sponge.	10.2 x 40.6	... do. ...	240	1,141	4.75	.90	14,400	20–26
25934	Gas-swept magnesium reduced titanium sponge.	10.2 x 40.6	... do. ...	190	588	3.08	2.26	14,500	32
26157	Leached and dried sodium-reduced titanium sponge.	10.2 x 40.6	... do. ...	104	258	2.49	2.93	13,200	40
26253	Vacuum distilled magnesium-reduced titanium sponge.	7.6 x 40.6	... do. ...	211	693	3.28	2.41	15,000	30
26266	Ti–5Al–2.5 Sn forged bar.	4.1 x 20.5 ²	... do. ...	120	517	4.29	1.8	13,000	34
26282	Ti–6Al–4V forged bar.	8.3 x 40.0	... do. ...	165	736	4.47	1.8	15,000	32
26297	Gas-swept magnesium-reduced titanium sponge.	5.1 x 40.6	... do. ...	156	500	3.19	2.24	13,500	32
26457	Gas-swept magnesium-reduced titanium sponge.	20.3 octagon	... do. ...	293	573	1.96	2.50	12,000	30
26470	Vacuum-distilled magnesium-reduced titanium sponge.	20.3 octagon	... do. ...	152	667	4.40	1.48	13,000–13,500	27–28

¹ All ingots were melted in the 17.8-by 50.8-cm slab-shaped crucible except SA 26457 and SA 26470, which were melted in a 30.5-cm diameter round crucible.

² Electrode was offset in crucible to provide equal spacing on 3 sides with wider spacing on 4th side.

since the number of ingots melted was not great.

Figure 60 shows an ingot (SA 25835) prepared by electroslag melting, and figure 61 shows the internal structure of this same ingot. Starting

material for this ingot was leached-and-dried titanium sponge prepared by magnesium reduction. Figure 62 shows the internal structure of an ingot prepared from this same sponge by double



Figure 60.—Slab-shaped ingot SA 25835 prepared by electroslag melting leached and dried titanium sponge.

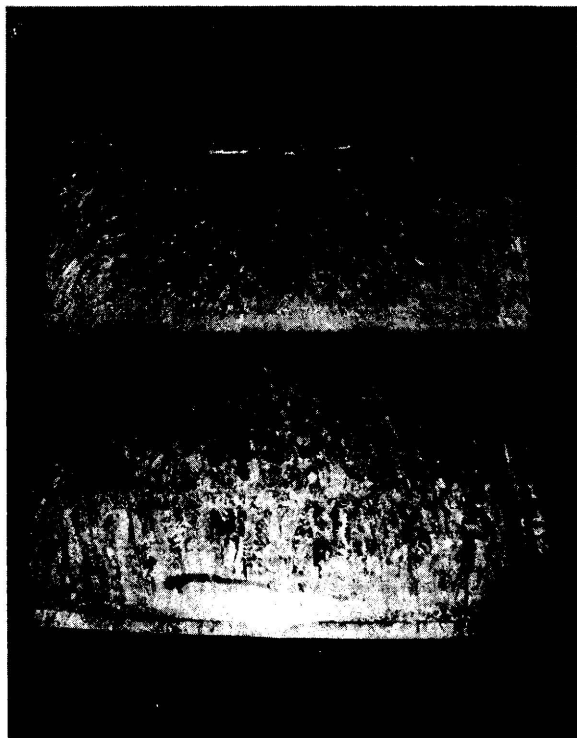


Figure 61.—Etched internal surface of ingot SA 25835 prepared by electroslag melting leached and dried titanium sponge.

vacuum-arc melting in the slab-shaped crucible. Considerably more subsurface porosity is evident in the ingot prepared by vacuum-arc melting.

No significant differences were noted in the impurity content of ingots produced in the prototype furnace and ingots prepared in the small-scale tests. The same general trends were noted with regard to hydrogen and fluorine contamination for ingots from the prototype furnace as for small-scale ingots.

One trend which was more noticeable in the large-scale, slab-shaped ingots was an increase in hardness at the bottom of the ingots. The hardness pattern for the ingot shown in figures 60 and 61 is displayed in figure 63. This figure shows hardness values on the plane through the center of the ingot and parallel to the 50.8-cm axis of the cross section. The increased hardness noted along the lower part of the ingot is attributed to impurities in the flux. During melting of this ingot, all of the flux was added to the crucible prior to the start of melting, and the first titanium melted gettered the flux and caused

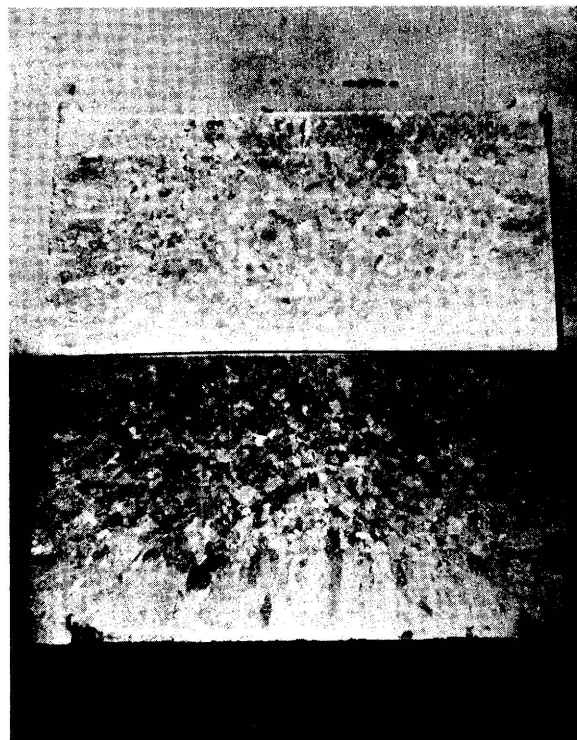


Figure 62.—Etched internal surface of ingot SA 25877 prepared by double vacuum-arc melting leached and dried titanium sponge.

an increase in impurity content at the bottom of the ingot.

Good-quality ingots were prepared by electroslag melting in a 30.5-cm-diameter round crucible. Figure 64 is a photograph of an ingot prepared by melting vacuum-distilled sponge in calcium fluoride flux. Some roughness of the sidewalls of this ingot is evident; however, for the most part, the sidewalls were considered satisfactory for forging with only a minimum of machining. Figure 65 shows a similar ingot electroslag melted from a domestic sponge.

While the ingot prepared from domestic sponge did not have smooth sidewalls, the internal structure was sound. The sidewalls were much rougher on the upper half of the ingot than on the lower half, presumably due to depletion of the slag cover during melting. As in all other runs in the prototype furnace, the entire charge of slag was placed in the crucible at the start of the run. The run was sufficiently unstable to cause frequent eruptions of the slag pool with a considerable resultant loss of flux

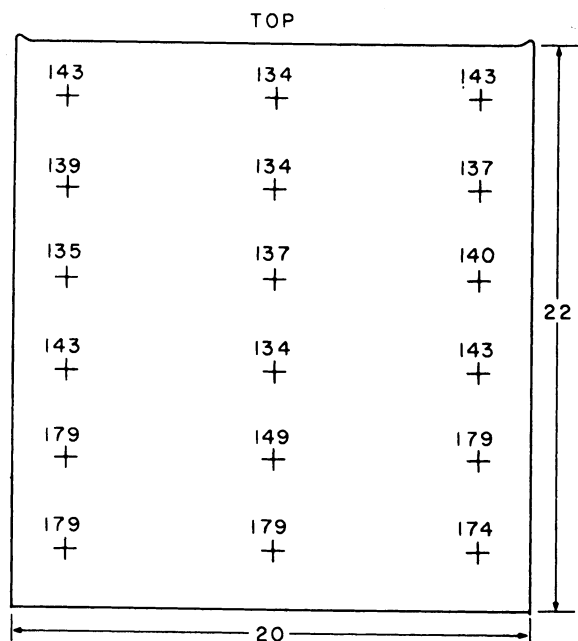


Figure 63.—Variation in Brinell hardness as measured on the interior surface of electroslag-melted ingot SA 25835 (leached-and-dried sponge).

from the crucible. It is also possible that the flux became sufficiently contaminated with chlorides by the time the run was half-finished to cause the sidewall roughness noted. No differences in furnace operation were noted that could explain the marked difference between the upper and lower ingot halves. A similar change in ingot sidewall quality as a function of ingot length was not observed during melting of slab-shaped ingots.

SOVIET RESEARCH

Morozov and coworkers (2) have reported electroslag melting titanium alloy slab-shaped ingots weighing 500 kg with outside dimensions of 20 by 80 by 70 cm in a three-electrode automatic furnace. A two-section water-cooled copper mold was used. Furnace power was supplied from a three-phase, 380-volt ac (1,350-kva) power transformer. Voltages between 21 and 50 volts at 15,000 amperes for each of the furnace electrodes

are possible. Minimum cooling water flow was $70\text{ m}^3\text{ hr}^{-1}$. The furnace is loaded in a similar manner to that described for our work, although some of the flux remains in a feeding hopper. The furnace is pumped and backfilled with argon to 0.1 atm.

Results of one slab-shaped ingot appeared comparable to those achieved in our laboratory. Uneven surfaces were attributed to erratic feeding rates of one of the three electrodes.

When comparing problems in small-scale and large-scale electroslag melting, there are several areas in which it is difficult to extrapolate from one to the other. Among these are the electrode temperature field, which is probably one dimensional on a small-scale unit and two dimensional (axial and radial distributions) on a large-scale unit. Mitchell, Szekely, and Elliott (1) consider that the electrode-flux and ingot-flux interfaces in small-scale units can be considered as isopotential contours. This is not believed to be the case in larger units where voltage gradients must be taken into account. Another area of scale-up difficulty lies in the chemical and electrochemical processes occurring in the flux and at the metal-flux interfaces. Such data can be obtained empirically for a small unit, but scale-up extrapolations are risky because the amount of polarization (for example, in dc reverse polarity operations) is affected by the local current density, and by the relative motion of the flux and metal, which in turn are influenced by the flux volume and areas of electrode and ingot exposed to the molten flux.

CONCLUSIONS

The following recommendations for industrial use are made as a result of experience gained with the prototype furnace:

1. Large-scale round ingots, suitable for direct fabrication, can be prepared from vacuum-distilled titanium sponge by electroslag melting in purified calcium fluoride. A liquid flux starting procedure would be superior to starting with a solid flux, but ingots can be prepared by the methods used in this work. Ingots prepared from domestic sponge containing large amounts of volatiles will not be satisfactory for direct conversion to plate and sheet.
2. Power requirements for electroslag melting are greater than for vacuum-arc melting. An arc current slightly in excess of 400 amperes per centimeter (1,000 amperes per inch) of

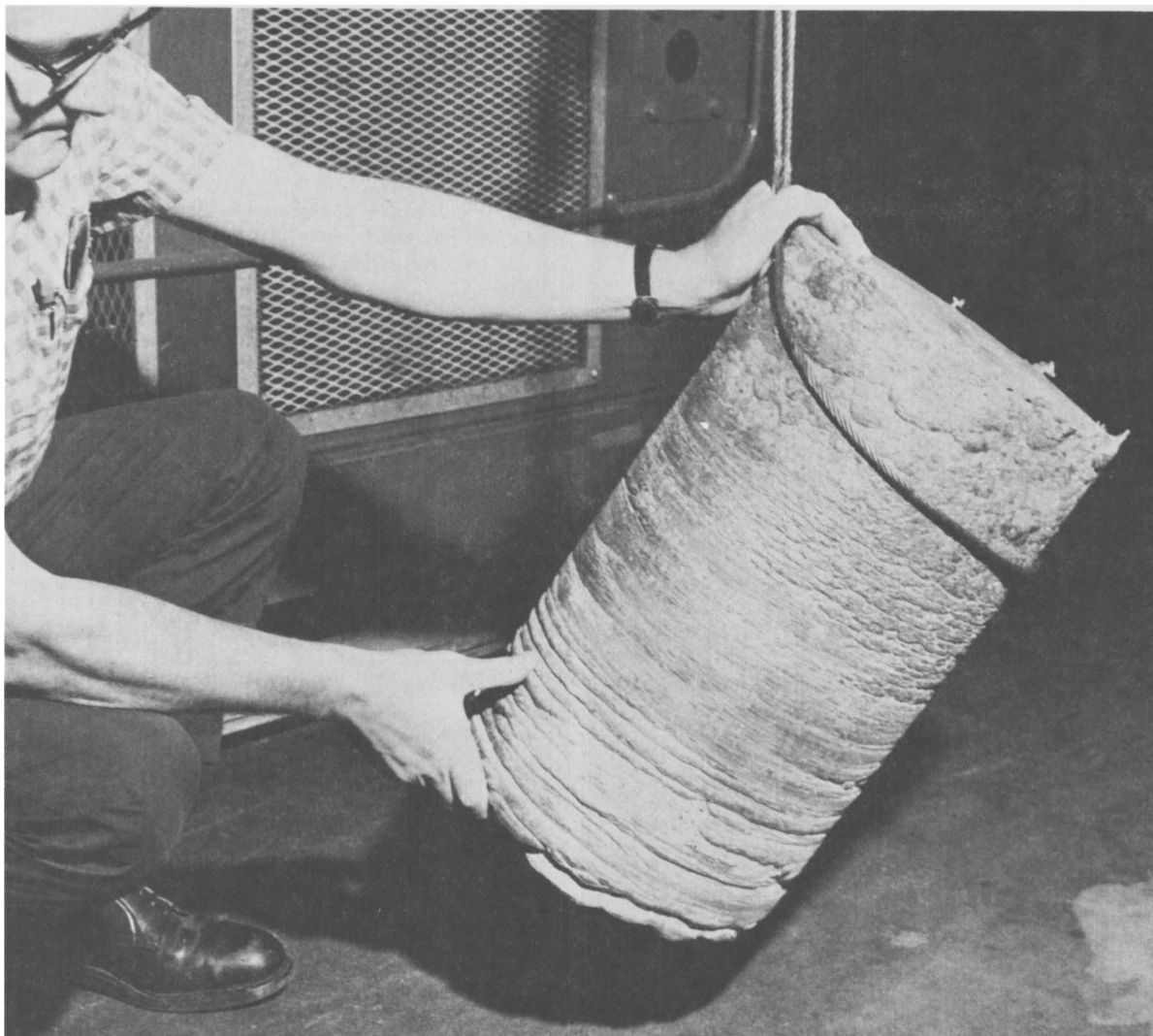


Figure 64.—Electroslag-melted 30.5-cm-diameter (12-in.) ingot of vacuum-distilled titanium sponge.

ingot diameter serves as a guide in determining requirements for electroslag melting. For example, a 10.2-cm-diameter ingot requires approximately 4,000 amperes of melting current at 24 volts potential; a 15.2-cm-diameter ingot was melted with excellent results at a melting current of 6,500 to 6,800 amperes at 22 to 24 volts potential. The best 30.5-cm-diameter ingot was melted at 13,000 to 13,500 amperes at 27 to 28 volts potential; however, the melting rate for this run was very low, and better results might have been obtained at a higher power input.

3. Slightly better slab-shaped ingots were obtained with electrodes of smaller cross section. The results obtained were not clearly

defined, however, because the improvement obtained was relatively minor. Similar studies with large-scale round ingots were not conducted.

4. Flux used for electroslag melting of titanium must be carefully pretreated prior to use. Sufficient flux must be maintained in the crucible to allow melting at up to 30 volts potential. When the flux depth is too shallow, the electrode cannot be submerged in the flux without reducing the melting potential to such a low value that the melting rate is very low. The 15.2-cm ingot was melted with a minimum flux depth of 3.8 cm, and sufficient flux was maintained in the large-scale runs for at least 7.6 cm of flux.

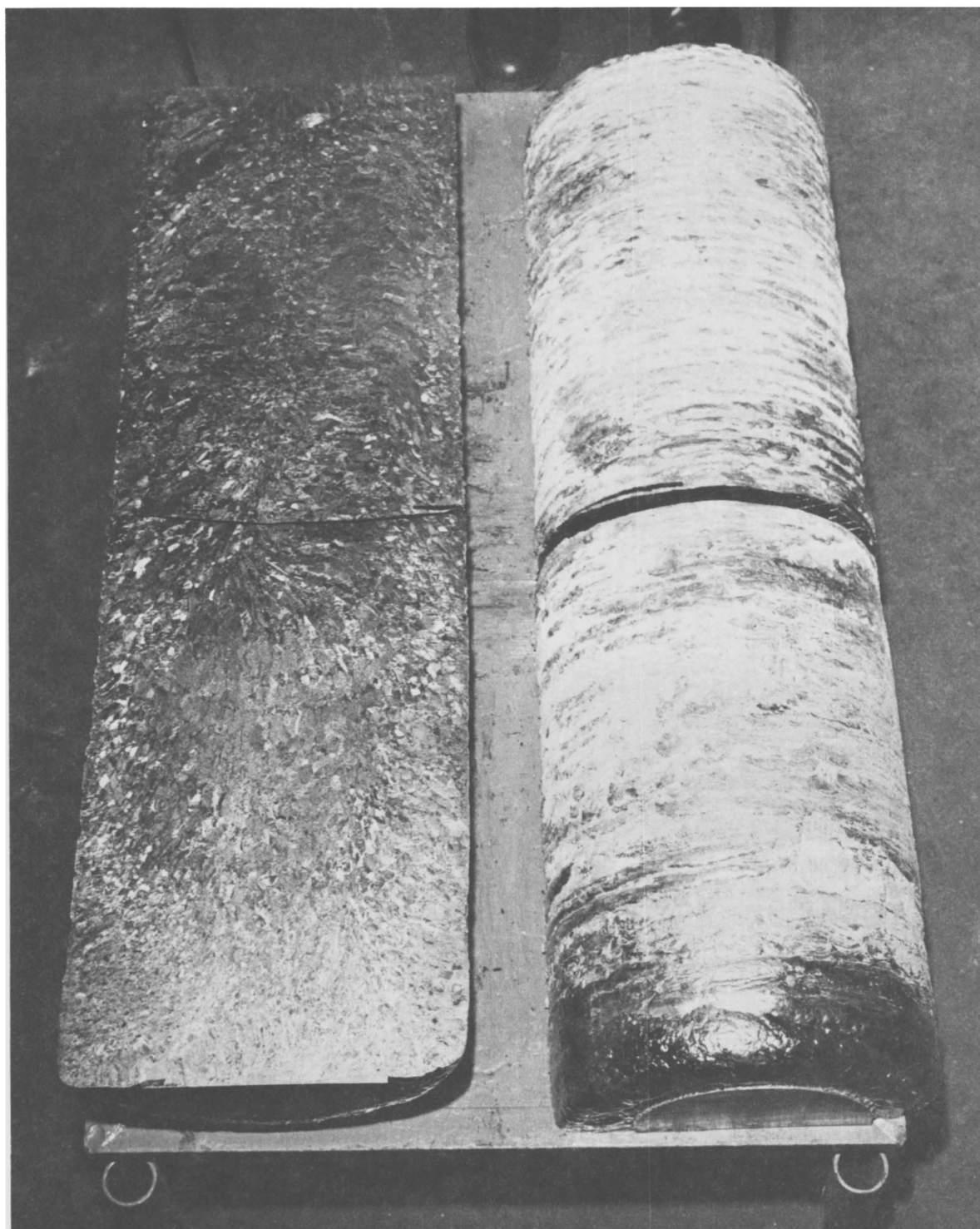


Figure 65.—Electroslag-melted 30.5-cm-diameter, (12-in.) ingot of gas-sweep-processed titanium sponge.

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2. Morozov, E. I., et al. (Electroslag Smelting of Titanium Ingots). Titanium in Industry, Oborogiz, Moscow, 1961, pp. 314-326 (U.S. Dept. of Commerce, JPRS 16,144, 1962).

⁴ The title enclosed in parentheses is a translation from the language in which the item was published.

CHAPTER 9.—PROPERTIES OF ELECTROSLAG AND VACUUM-ARC MELTED TITANIUM¹

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This chapter presents mechanical properties obtained for wrought shapes formed from electrosag-melted ingots, and compares the properties with those obtained for like shapes from double-vacuum-arc-melted material. The preparation of ingots and the working of ingots to shapes are described. Electrosag-melted material contains residual fluorine from the flux which could affect the corrosion resistance of titanium. Microstructures of worked material are examined. A summary of available Soviet results is also presented.

PREPARATION OF INGOTS

Electrodes for both vacuum-arc melting and electrosag melting were prepared from pressed compacts of vacuum-distilled titanium sponge as described in chapters 7 and 8.

Some electrodes were electrosag-melted into 10.2-cm (4-inch) diameter ingots weighing 7.3 kg (16 pounds); otherwise 17.8- by 50.8-cm (7- by 20-inches) slab-shaped ingots were prepared. The vacuum-arc-melted ingots were all 10.2 cm in diameter and were sectioned, rewelded into electrodes, and remelted. Electrosag-melted ingots were not remelted, an advantage claimed for this process. Vacuum-arc-melting practice is to double-melt to remove impurities and porosity from the ingot. Schematic drawings of both the electrosag and vacuum-arc furnaces are given in

chapters 7 and 8. Melting procedures are also given in these chapters.

Arc melts were made with 3,800 dc amperes and 28 to 30 volts. Ten centimeter (4 inch) ingot electrosag melts were made with 4,500 dc amperes and 20 to 22 volts. For the slab ingots, the current was 13,000 to 14,000 amperes at 32 volts dc. The initial practice to control shrink-pipe in the 10.2-cm electrosag-melted ingots was to gradually decrease the current to 3,000 amperes or less at the completion of the melt; however, the insulating effect of the slag adequately controls the shrinkage cavity so melts are now terminated when electrodes are consumed. Power utilization from vacuum-arc melting was 3 kwhr kg^{-1} at a melting rate of 1.4 kg min^{-1} . Ten centimeter (4 inch) electrosag-melted ingots were melted at a rate of 0.9 kg min^{-1} with power utilization at 1.5 kwhr kg^{-1} . The melting rate for the slab ingots was 0.9 to 2.7 kg min^{-1} at 1.8 to 4.4 kwhr kg^{-1} . All melts, both vacuum-arc and electrosag, were made with electrode negative polarity.

The flux for melting was prepared from reagent-grade calcium fluoride, since this flux offers the most favorable operating conditions and produces ingots which are most readily amenable to testing. Flux preparation has been described in chapter 7.

Examination of ingot structures showed the ingots were sound except for a shrinkage cavity at the top of the vacuum-arc-melted ingots and relatively homogeneous. The bottom of the ingots (first metal melted) tended to have a slightly higher impurity content. This was attributed to residual impurities from the furnace components (and also from the flux charge in the case of electrosag-melted ingots).

Typical analyses for ingots prepared from vacuum-distilled sponge are given in chapter 7.

FABRICATION

Ten-centimeter (4-inch) diameters ingots pro-

¹ Adapted from Topical Report to U.S. Army Materials and Mechanics Research Center, Watertown, Mass., USBM-RC-1351, 1969; Trans. Am. Foundrymen's Soc., v. 77, 1969, pp. 353-359; The Science, Technology, and Application of Titanium, ed. by R. Jaffee and N. Promisel, Pergamon Press, Oxford and New York, 1970, pp. 67-74.

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duced by electroslag melting were fabricated to plate, sheet, and rod without prior conditioning of the ingot sidewalls. Ingots formed by double vacuum-arc melting were machined before forging. Shrinkage cavities were removed by cropping the tops from ingots prepared by vacuum-arc melting. The electroslag-melted ingots were free of shrinkage defects, but contained unmelted sponge particles at the bottom. These were removed by cropping the bottoms. A uniform size of ingots for forging was maintained by cropping both ends from all ingots.

Fabrication procedures were the same for ingots from both melting processes. Ingots were heated for 2 hours at 900° C and then press forged to 5.1 cm (2 inches) thick by 10.2 cm (4 inches) wide in three workings with reheats between workings. The forgings were then reheated and rolled to 2.54-cm (1 inch) thickness. After conditioning by sand blasting, the slabs were reheated to 900° C for 30 minutes and cross-rolled to plate 1.3 cm (1/2 inch) thick by 20.3 cm (8 inch) long. Breakdown forging to obtain rod was similar. Ingots were initially forged to bars 2.54 to 3.81 cm (1 to 1 1/2 inches) in cross section and then forged round. Samples for impact tests were removed from sections of the 1.3 cm-thick plate. Figure 66 shows the layout used to obtain samples from the plate and the condition of the plate.

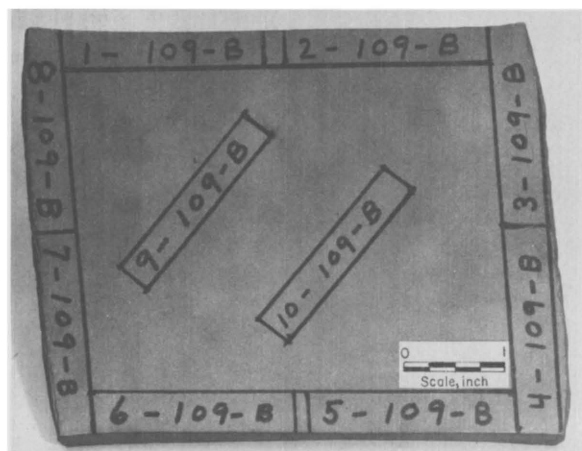


Figure 66.—Layout for cutting coupons for machining Charpy V-notch impact specimens from rolled plate.

Secondary working of plate and rod was accomplished by heating to 850° C for 30 min, working from one to three passes, and reheating 10 minutes to temperature. Reduction, in either the rolling mill or rotary swage, was approximately 10 percent per working pass. After working to the final dimensions, 2.54-cm (1 inch) diameter for rods and 0.6-cm (1/4-inch) thickness for plates, the materials were alpha-annealed at 700° C for one-half hour. Hot-rolled and cold-rolled sheet, 0.16 cm (1/16 inch) in thickness, was prepared from 0.6-cm-thick plate. Hot rolling was accomplished between 800° and 850° C. Material for cold rolling was hot-rolled to adjust thickness and then annealed at 700° C for one-half hour. Cold-rolling reductions, ranging from 10 to 50 percent, were made by taking 10-percent reductions each pass.

The large slab ingots were sectioned vertically through the center to produce plate of 1.27-cm (1/2-inch) thickness. The plates were sectioned to produce coupons about 1.27 cm (1/2 inch) square by 7.6 cm (3 inches) long. The layout used for sampling is shown in figure 67. The Charpy V-notch specimens were machined from these coupons. All Charpy specimens were carefully machined to remove equal amounts of material from their ends and each face. This was done to lessen any chances for surface reaction during sawing or working.

A few smaller slab-shaped ingots electroslag melted from two sponge sources (see chapter 7) were also fabricated for testing. These ingots were side-forged at 700° C from as-cast slabs 7.6 by 16.5 by 19.1 cm (3 by 6 1/2 by 7 1/2 inches) to billets 3.8 by 12.7 by 45.7–50.8 cm (1 1/2 by 5 by 18–20 inches). After forging through five passes, the billets were air-cooled. Some surface grinding of isolated areas was required before the rolling operation. The billets were reduced through the rolls at 700° C to final sheet thickness of 0.25 cm; final sheets were 50.8 cm wide by 127 cm long. Cross rolling was employed to obtain the width and to keep the sheet flat.

TENSILE TESTS

For 10.2-cm-diameter ingots, tensile properties were obtained for swaged rod and rolled plate in the alpha-annealed condition, and for sheet in both hot- and cold-rolled conditions. Specimens were prepared and tested according to the procedures recommended by the American Society for Testing and Materials. Specimens from rods were 1.27-cm (1/2-inch) diameter rounds with 5.1-

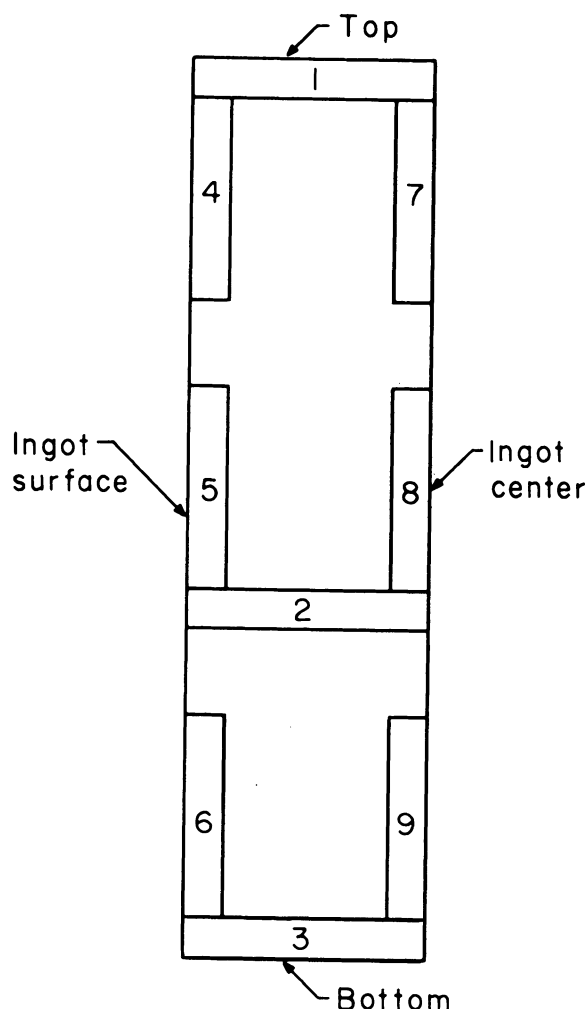


Figure 67.—Layout for cutting coupons for machining Charpy V-notch specimens from as-cast sections removed from slab ingot 17.8 by 50.8 cm (7 by 20 in.) in cross section.

cm (2-inch) gage length. Specimens from plate and sheet were 1.27 cm wide with a 5.1-cm gage length. The specimens were tested with a 27,270-kg (60,000-pound) Baldwin tensile-testing machine at a straining rate of 0.05 cm/cm/min.

Results from room-temperature tests for rod and plate specimens are shown in table 25. Tensile fractures for the two materials, vacuum-arc-remelted and electroslag-melted, were similar.

Transverse sheet tensile properties are compared in figures 68 and 69 for material prepared by the two melting processes. The zero percent cold-work data were for hot-rolled sheet; the rest of the data were obtained on sheet cold

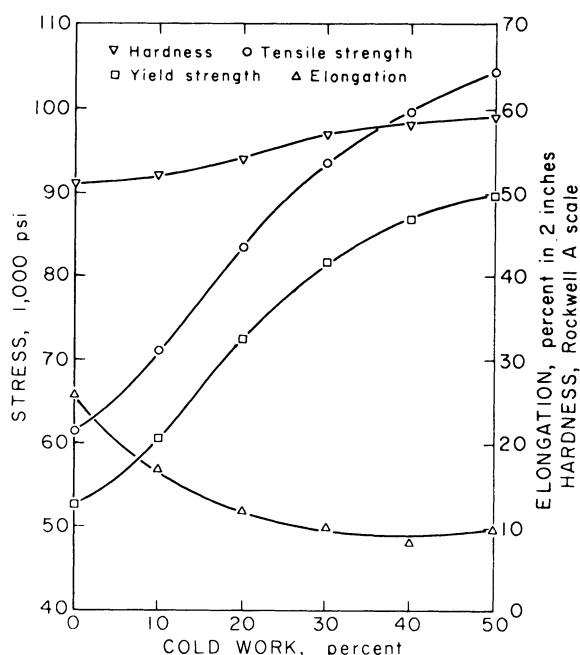


Figure 68.—Transverse tensile properties and hardness of 0.16-cm (1/16-in) sheet, vacuum-arc-remelted.

rolled from material in alpha-annealed condition. Longitudinal tensile properties were also obtained for the rolled sheet. Strength properties were slightly lower, and elongation values showed corresponding increases.

The tensile properties of products prepared from electroslag-melted ingots compare very favorably with those of products prepared from vacuum-arc-remelted ingots and appear acceptable.

For the small slab-shaped ingots, standard flat tensile specimens 0.64 by 2.54 cm (1/4- by 1-inch) were machined from each sheet. Specimen locations were selected to represent both center and outside at top, middle, and bottom sites, and were taken both transversely and longitudinally to the final roll direction. Duplicate specimens were taken from each site so that a total of 12 sites and 24 coupons were machined from each sheet.

Test results (table 25) showed a slight increase in ultimate tensile strength and yield strength from top to bottom with a corresponding decrease in reduction in areas. This was particularly noticeable in the material from vacuum-distilled sponge. No difference could be detected from outside to inside nor in roll direction. The

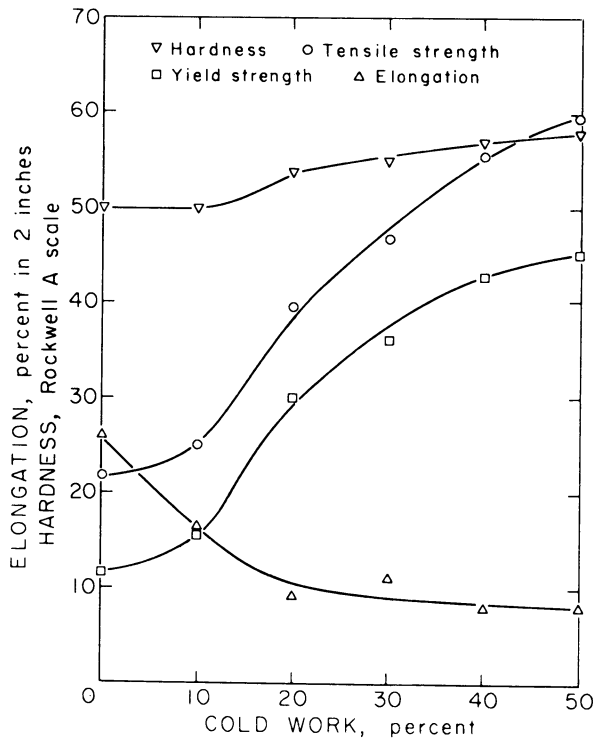


Figure 69.—Transverse tensile properties and hardness of 0.16-cm (1/16-in) sheet, electroslag-melted.

data were quite uniform within each sheet but differed by about 1,400 kg cm⁻² (20,000 psi) ultimate strength between the two ingots.

BEND TESTS

The room-temperature minimum bend radius was determined for sheet from the 10.2-cm diameter ingots in the as-hot-rolled condition, and sheet reduced 50 percent by cold rolling. Specimens were 6.4 cm (2½ inch) long, 1.27 cm (½ inch) wide, and 0.16 cm (1/16 inch) thick. The specimens were bent in a fixture with a 2.54-cm (1-inch) span between the supports. Bending rate was 0.5 cm min⁻¹ of punch travel. The radius of the punch was increased successively until no evidence of failure could be detected on the tensile side of the specimen after a 90° bend angle. The bent specimens were examined for failure at a magnification of 10. Results are listed in table 26 for both longitudinal and transverse specimens. The bend axis was perpendicular to the rolling direction for longitudinal specimens and parallel to the rolling direction for transverse specimens.

The bending character at room temperature appears to be superior for vacuum-arc-melted material, especially for the hot-rolled sheet. The difference in bending ductility indicated for the

Table 25.—Average tensile properties of plate, sheet, and swaged rod

Ingot	Orientation	Tensile strength, psi ¹	Yield strength, 0.2 percent offset, psi ¹	Elongation, percent in 2 inches	Reduction in area, percent
Rod from 10-cm (4-inch) ingots: ²					
Vacuum-arc-remelted ..	Longitudinal	57,000	37,300	40	65
Electroslag-melted	 do.	60,000	45,000	34	60
Plate from 10-cm (4-inch) ingots: ²					
Vacuum-arc-remelted ..	Longitudinal	57,000	41,300	35	68
	Transverse	57,400	47,300	33	63
Electroslag-melted	Longitudinal	55,200	40,600	37	66
	Transverse	54,500	43,400	37	67
Sheet from small slab-shaped ingots: ³					
Electroslag-melted from vacuum-distilled sponge.	Longitudinal	57,600	45,100	35	73
	Transverse	55,300	45,100	31	72
Electroslag-melted from magnesium-reduced, leached-and-dried sponge.	Longitudinal	81,200	72,400	22	50
	Transverse	81,100	71,400	21	52

¹ To convert to kg/cm², multiply by 0.0703.

² Average of at least 4 tests.

³ Average of 12 tests.

two materials might have resulted from ingot preparation before forging. Ingots obtained by vacuum-arc melting were machined. Electroslag-melted ingots were not.

IMPACT TESTS

Impact strengths were determined at room temperature on a Riehle impact tester using 0 to 250 capacity range. The specimens were Charpy V-notch type, 10 by 10 by 55 mm. The V-notch was 2 mm deep and centered on a face. The results are summarized in tables 27 and 28. From these tables it can be seen that electroslag-

melted material possesses significantly lower impact strength than vacuum-arc-melted material. Among the various sponge sources for electroslag melts, vacuum-distilled sponge yielded material with the best impact strength; leached-and-dried material was significantly worse.

SOVIET RESULTS

Soviet investigators have reported results of mechanical property tests on titanium and titanium alloy electroslag and double-vacuum-arc-remelted as-cast ingots. Tensile strength, elongation, and reduction in area were nearly identical

Table 26.—Minimum bend radius for 0.16-cm (1/16-inch) sheet specimens tested at room temperature

Material	Condition	Orientation	Minimum bend radius ¹
Vacuum-arc-remelted	Hot-rolled	Longitudinal	1t
		Transverse	2t
	Cold-rolled	Longitudinal	4t
		Transverse	5t
Electroslag-melted	50 percent	Longitudinal	3t
		Transverse	3t
	Hot-rolled	Longitudinal	5t
		Transverse	>4t

¹ Minimum bend radius was defined as the minimum radius, expressed in units of sheet thickness (0.16 cm or 1/16 inch), of the mandrel around which the sheet was bent to a full 90° bend angle without evidence of failure when observed at a magnification of 10 diameters.

Table 27.—Impact strengths of plates fabricated from titanium ingots consolidated by electroslag and vacuum-arc melting

Coupon No. (fig. 66)	Heat No. ¹	Melting method	Impact strength, ft-lb	Coupon No. (fig. 66)	Heat No. ¹	Melting method	Impact strength, ft-lb
1	897-B	ES	66	6	897-B	ES	75
	097	ES	53		097	ES	63
	109-B	VA	150		109-B	VA	152
2	897-B	ES	49	7	897-B	ES	57
	097	ES	29		097	ES	62
	109-B	VA	137		109-B	VA	205
3	897-B	ES	48	8	897-B	ES	45
	097	ES	42		097	ES	79
	109-B	VA	137		109-B	VA	155
4	897-B	ES	64	9	897-B	ES	81
	097	ES	79		097	ES	58
	109-B	VA	194		109-B	VA	219
5	897-B	ES	64	10	897-B	ES	83
	097	ES	48		097	ES	59
	109-B	VA	219		109-B	VA	143

ES=Electroslag. VA=Vacuum arc.

¹ 897-B and 109-B designations indicate 10-cm (4-inch) diameter ingot melted from 7.6- by 17.8-cm vacuum-distilled sponge. 097 designations indicate 3- by 7-inch slab-shaped ingot melted from vacuum-distilled sponge.

Table 28.—*Effect of sponge on the Charpy V-notch impact strength of electroslog-melted 18- by 50-cm (7- by 20-in) slab-shaped titanium ingots, as-cast*

Coupon No. (fig. 67)	Heat No.	Impact strength, ft-lb	Coupon No. (fig. 67)	Heat No.	Impact strength, ft-lb
1	¹ 25835	9	6	¹ 25835	10
	² 25886	53		² 25886	75
	³ 25934	22		³ 25934	30
	⁴ 26157	3		⁴ 26157	3
2	¹ 25835	14	7	¹ 25835	9
	² 25886	101		² 25886	81
	³ 25934	23		³ 25934	19
	⁴ 26157	3		(⁶)	—
3	¹ 25835	66	8	¹ 25835	13
	² 25886	108		² 25886	131
	³ 25934	22		³ 25934	19
	⁴ 26157	3			
4	¹ 25835	8	9	¹ 25835	6
	² 25886	72		² 25886	64
	³ 25934	26		³ 25934	16
	⁴ 26157	3			
5	¹ 25835	10			
	² 25886	91			
	³ 25935	27			
	⁴ 26157	3			

¹ Mg-reduced, leached-and-dried sponge.

² Mg-reduced, vacuum-distilled sponge.

³ Mg-reduced, gas-swept and/or water-leached sponge.

⁴ Na-reduced, leached-and-dried sponge.

⁶ There were only 6 specimens made from the Na-reduced, leached-and-dried sponge.

for metal melted by the two process, although electroslog metal was shown to possess a slightly lower impact strength (2). However, electroslog melting a Ti-8Mn alloy produced ingots with better properties than did double vacuum-arc melting. Additions of aluminum (1.25–2.5 percent) and manganese (0.8–1.5 percent) increased the tensile strength and decreased the impact strength of as-cast electroslog-melted metal (1). Vacuum annealing after electroslog melting exerts a minimal effect on the ductility and impact strength of the metal, as does the shape of the as-cast ingots (1). If titanium is electroslog-melted in an open mold, followed by annealing and forming, mechanical properties are nearly identical to those of the electrode material (3).

CORROSION TESTS

To determine if the fluorine impurity found in electroslog-melted titanium (see chapter 7) is detrimental to the corrosion resistance normally observed in vacuum-arc-melted material, 2.9-cm (1 $\frac{1}{8}$ -inch) square coupons sheared from 0.16-cm

(1/16-inch) thick sheet that had been cold-rolled to 50 percent of the original thickness and vapor blasted, were corrosion-tested at the Bureau of Mines College Park Metallurgy Research Center. The electroslog-melted material contained approximately 100 ppm of residual fluorine, whereas the vacuum-arc-remelted titanium contained no fluorine. Testing media were air-aerated substitute ocean water, which normally does not corrode titanium, 10 percent air-aerated H₂SO₄ solution, and 5 percent H₂SO₄ helium-aerated solution. The H₂SO₄ solutions normally corrode titanium very slowly. The results are summarized in table 29. It can be seen that electroslog-melted and vacuum-arc-remelted titanium have essentially the same corrosion behavior in these environments. Both types of titanium are inert in substitute ocean water and corrode at moderate rates in the sulfuric acid solutions.

MICROSTRUCTURES

The structures of the titanium were observed

in hot-rolled, annealed, and 50-percent cold-rolled conditions. Samples were prepared by rough grinding and polishing using standard procedures. The structures were observed in the as-polished condition and as-polished and etched.

As-polished and etched photomicrographs are presented in figures 70 through 72. The microstructures of rolled plates in the annealed condition are shown in figure 70. The structures are essentially the same except for the inclusions that appear in the structure of the electroslag-melted material. Such inclusions are also present in the structures of sheet rolled from the electroslag-melted ingots (fig. 71). The alpha-annealed material was cold-rolled to a reduction of 50 percent in thickness. The resultant structures are shown in figure 72. Attempts to identify the inclusions shown in the photomicrographs were

not successful; however, the possibility of the inclusions being fluorides, carbides, or calcium was eliminated. Submicroscopic fluoride inclusions were revealed with the electron microprobe in the structures of all electroslag-melted material examined. The fluoride inclusions are not resolved in the photomicrographs shown.

The structures of the annealed plate (fig. 70) show very little transformed beta, while the hot-rolled sheet (fig. 71) has appreciable amounts, suggesting that the final working temperature was close to the alpha-beta transus. Grain size is essentially the same for similar shapes prepared from ingots melted by the two processes.

CONCLUSIONS

Rod, plate, and sheet fabricated from electroslag-melted ingots have been evaluated by com-

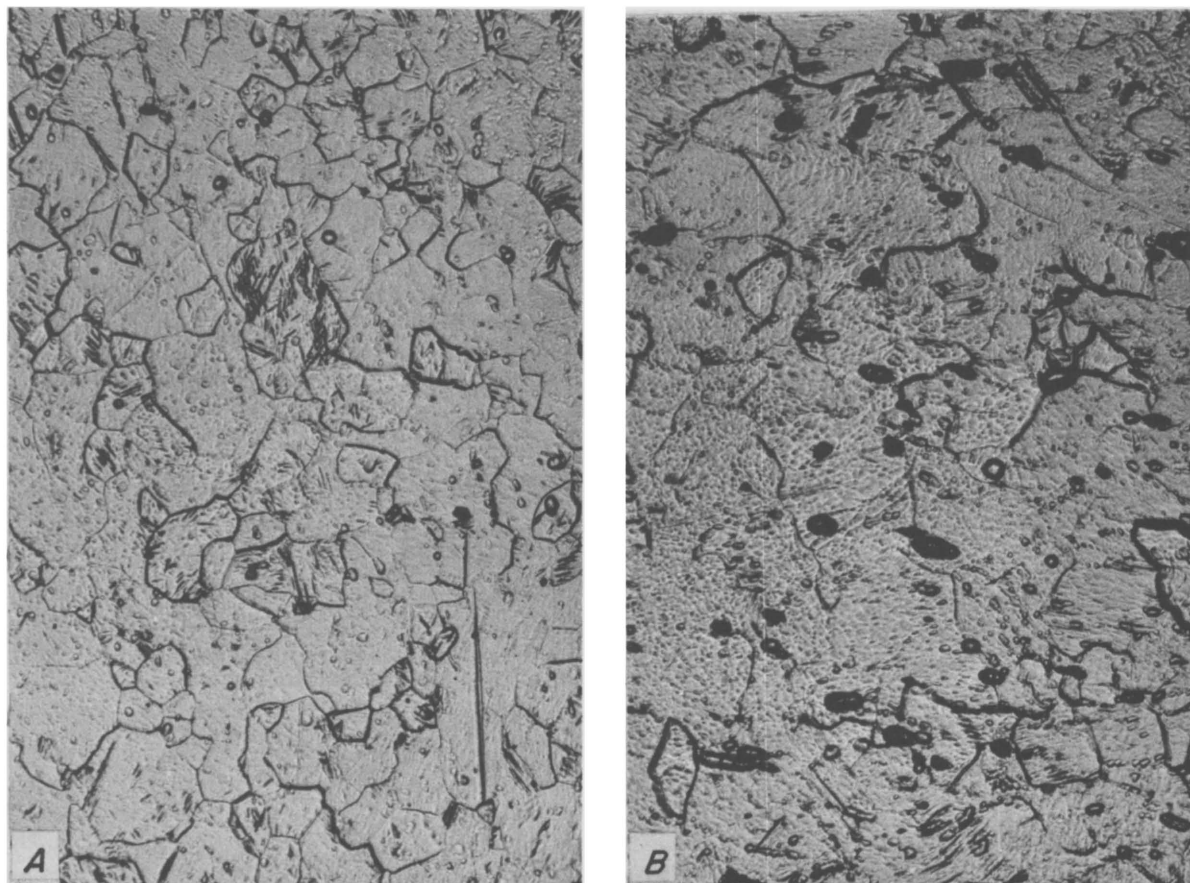


Figure 70.—Structures of hot-rolled plate annealed at 700° C for ½ hour (X 250). *A*, As-polished and etched, vacuum-arc-remelted; *B*, same, electroslag-melted

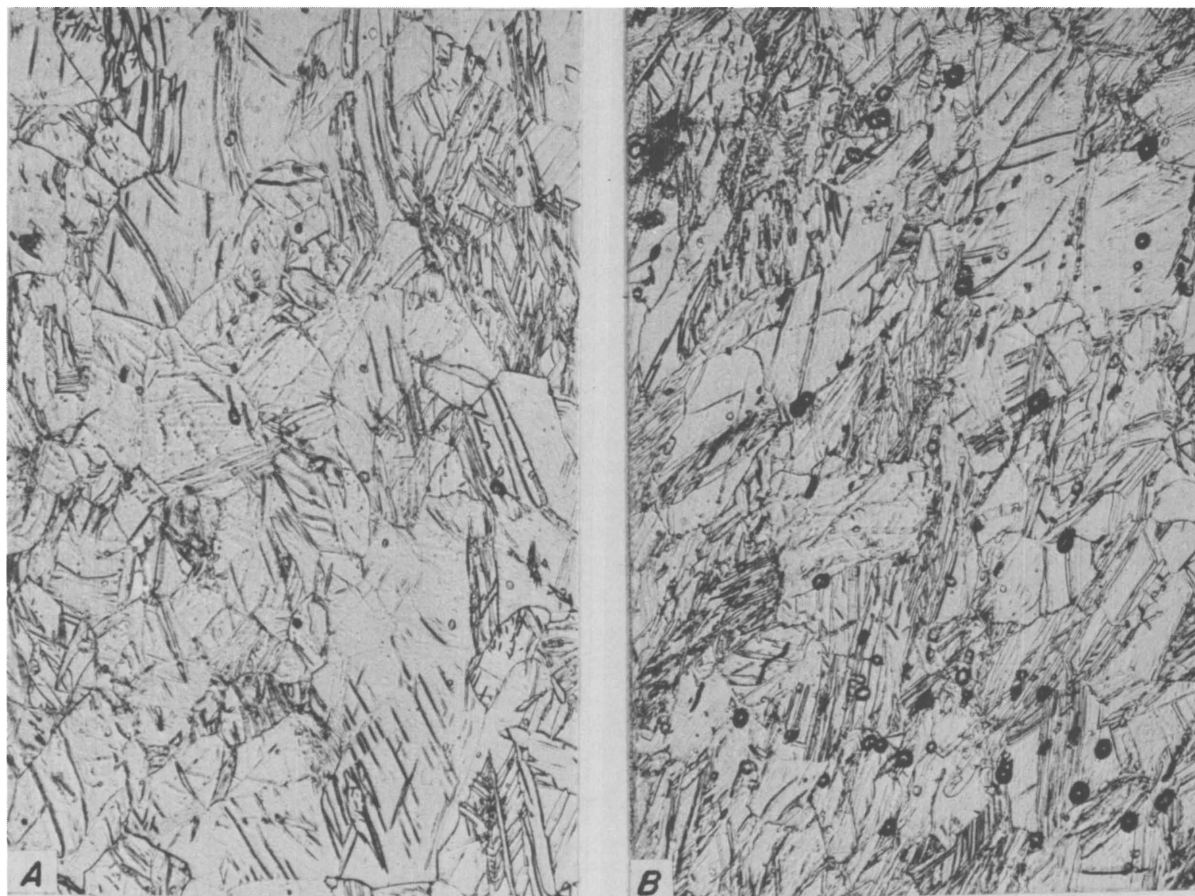


Figure 71.—Structures of hot-rolled sheet. (X 250) *A*, As-polished and etched, vacuum-arc-remelted; *B*, same, electroslag-melted.

Table 29.—Corrosion of titanium in substitute ocean water and sulfuric acid solutions at 35° C, 30-day tests ¹

Corrodent	Corrosion rate, mils/year	
	Vacuum-arc-remelted	Electroslag-melted
Substitute ocean water; air	0.0	0.0
10 percent H ₂ SO ₄ ; air	28.3 (26.1 to 30.1) ²	27.3 (24.0 to 29.0) ²
5 percent H ₂ SO ₄ ; He	16.6 (15.4 to 18.0) ²	19.0 (18.1 to 19.8) ²

¹ Tests conducted at the College Park Metallurgy Research Center, College Park, Md., by David Schlain, supervisory chemical research engineer.

² Range of values obtained on 4 specimens from each sheet condition.

paring properties to those of like shapes formed from double-vacuum-arc-melted material. Results indicate that for many applications electroslag-melted ingots should produce satisfactory results. Tensile and corrosion properties compared favorably for products wrought from ingots melted by the two methods. Sheet from vacuum-arc-remelted material had a slightly better bending character at room temperature. Impact strengths were markedly lower for the electroslag-melted titanium. Soviet authors have corroborated these findings. Inclusions present microscopically in electroslag-melted material were not identified. Submicroscopic inclusions of fluoride were present in electroslag-melted titanium.

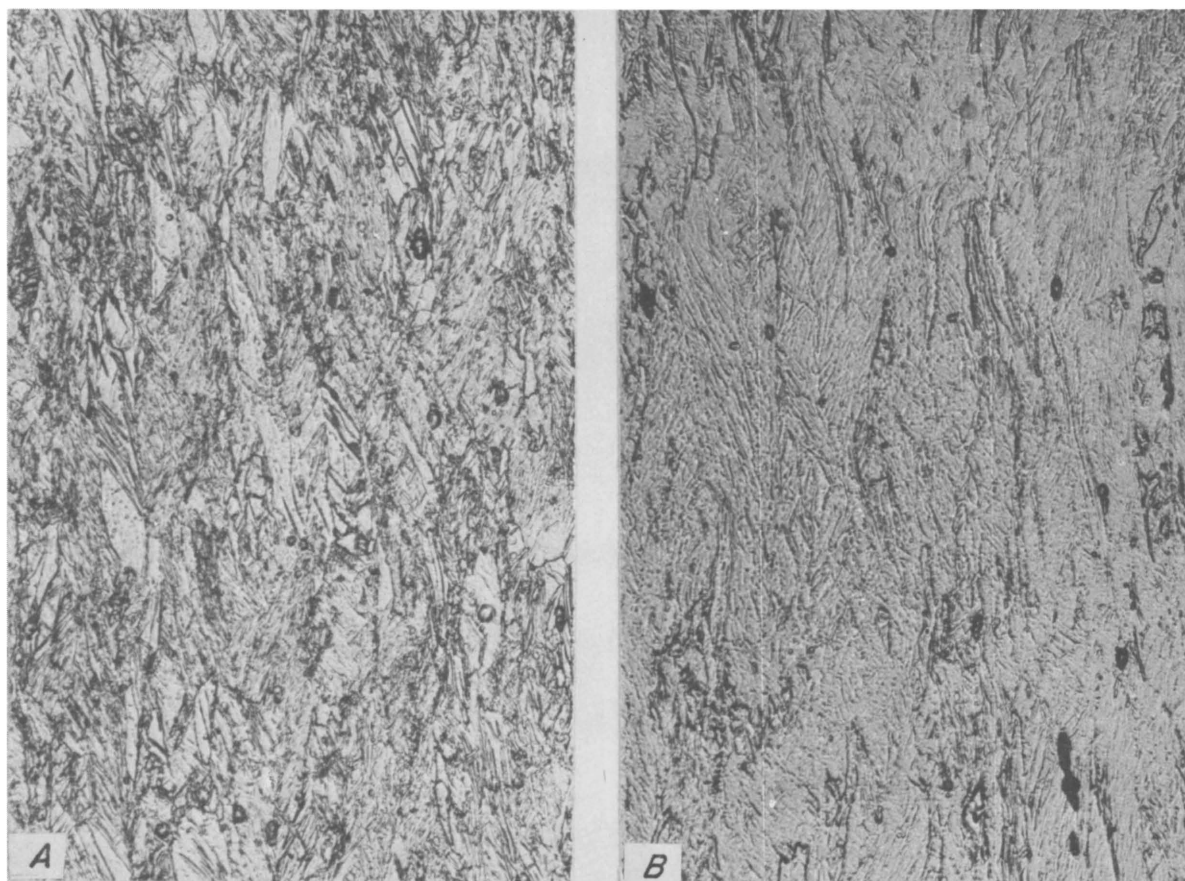


Figure 72.—Structures of sheet reduced 50 percent by cold rolling from alpha-annealed condition (X 500). *A*, As-polished and etched, vacuum-arc-remelted; *B*, same, electroslag-melted.

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⁶ Titles enclosed in parentheses are translations from the language in which the item was published.

CHAPTER 10.—ELECTROSLAG MELTING OF ZIRCONIUM¹

By R. H. Nafziger and E. D. Calvert²

Electroslag melting techniques have been successfully employed to produce high-quality ingots of superalloys and specialty-grade steels for several years. The electroslag process was believed to hold promise for melting reactive and refractory metals to give ingots with properties unattainable by consumable-electrode-arc melting or induction melting techniques. Results of titanium and molybdenum electroslag melting experiments in this laboratory have been reported in chapters 7, 8, 9, and 15. Zirconium was also thought to be a candidate for this melting technique since, to the authors' knowledge, no previous work concerning electroslag melting of this metal has been reported. Considerable interest was expressed by industrial representatives regarding the electroslag process as an alternative to conventional melting techniques for zirconium. Improvements in ingot chemistry to reduce or control impurities detrimental to ductility and mechanical properties were sought. In addition, electroslag melting produces smooth ingot surfaces which eliminate or reduce expensive machining prior to working, (1-2). A series of consumable-electrode zirconium electroslag melts was conducted under various operating conditions, and the products were evaluated with respect to impurities, resistance to corrosion, and mechanical properties to determine whether the aforementioned advantages of the electroslag process could be applied to zirconium.

MELTING TECHNIQUES

A modified vacuum-arc furnace equipped with a water-cooled copper crucible served as the melting vessel for all of the present work. The furnace is described in chapter 7. Three sources of zirconium provided the electrode material: (1) Compacted high-iron sponge, (2) fused-slab sections from production-grade evaluation ingots,

and (3) AEC reactor-grade sponge. The sponge was pressed at approximately 56×10^6 kg m⁻² (80,000 psi) to produce a ~5- by 5- by 25-cm (2- by 2- by 1-inch) compact. Three such compacts were butt-welded to form the electrode. Electrodes were made from the fused-slab sections by welding three sections together. Acid-grade prefused CaF₂ (1,000 grams per melt) or nominal 99.9 percent LaF₃ (1,600 to 1,800 grams per melt, prefused or recycled) provided the flux, which was loaded into the crucible and surrounded the electrode prior to furnace closure and pumpdown.

The melts were started by grounding the electrode to a zirconium base plate, switching the power on, manually separating the electrode and base plate, and then slowly increasing the power for electrode consumption after the flux was completely molten. The power was straight polarity (consumable electrode negative) or reverse polarity (positive) dc. Nominal melting parameters were 25 ± 4 and 31 ± 6 volts at $5,700 \pm 100$ and $4,900 \pm 200$ amperes for CaF₂ and LaF₃ flux melts, respectively. A typical melting rate with the LaF₃ flux was ~ 3.5 kg min⁻¹ (7.6 ± 0.1 lb min⁻¹) at approximately ~ 0.9 kwhr kg⁻¹ (0.4 kwhr lb⁻¹). Helium was employed either to backfill the furnace to approximately $\frac{1}{3}$ atm, or to sweep through the furnace at the same total pressure. Several vacuum-arc melts were conducted for comparison purposes.

INGOT QUALITY AND IMPURITIES

Ten-centimeter (4-inch) diameter zirconium ingots were produced by the electroslag process with a wide range of combinations of the aforementioned operating parameters. Figures 73, 74, and 75 illustrate typical as-melted ingots and show the variation in surface conditions as a function of melting conditions and electrode stock. When straight polarity dc was used for melting, surface quality was significantly better than that resulting from ingots melted with reverse polar-

¹ Adapted from Proc. 3d Internat. Symp. on Electroslag and other Special Melting Technology, ed. by G. K. Bhat and A. Simkovich, Pittsburgh, Pa., 1971, Pt. 2, pp. 253-279.

² Metallurgist, Albany Metallurgy Research Center, Bureau of Mines, Albany, Oreg.

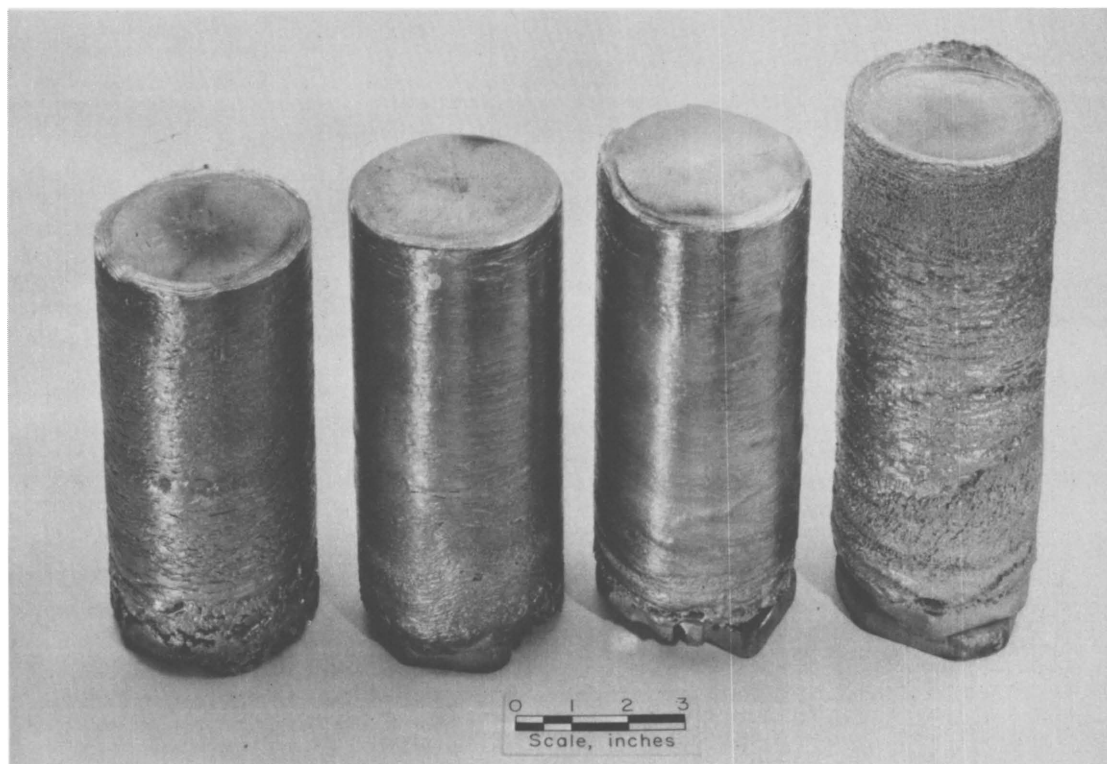


Figure 73.—Four-inch-diameter zirconium ingots electroslag melted under acid-grade CaF_2 and $\frac{1}{2}$ atm helium. The two ingots on the left were melted from high-iron sponge. The others were melted from fused slab sections. The two center ingots were melted with straight-polarity (consumable electrode negative) dc and those on the outside with reverse-polarity dc.

ity. Table 30 gives typical impurity analyses of the high-iron sponge electrode material, vacuum-arc-melted zirconium from this sponge, and ingots which were electroslag-melted from the high-iron sponge with the two flux compositions. Table 31 shows impurity data for the fused-slag electrodes and ingots melted from this material with two melting rates. Table 32 shows impurity contents for the reactor-grade zirconium sponge, vacuum-arc first melts and remelts from this sponge, and electroslag-melted ingots also from this sponge. Typical slag analyses before and after the melts are presented in table 33.

From these tables, it can be seen that purification of the metal by the slag is of minimal significance regardless of the operating parameters.

Additional observations regarding impurity changes from electrode to ingot during zirconium electroslag melting on the basis of all melt data, including some not given in tables 30–33, follow:

1. Electrode stock is the most significant tested

parameter for determining eventual ingot purity.

2. The melting rate plays essentially no part in determining ingot impurity levels.

3. The furnace atmosphere is more significant than dc polarity for ingot purity.

4. Electroslag melting does not improve ingot purity over vacuum-arc melting because (a) small amounts of fluorine are added to the ingot, (b) more volatile impurities (for example, hydrogen and magnesium) cannot escape as efficiently through the flux blanket, and (c) the flux tends to take up relatively small amounts of the melted metal.

INGOT HARDNESS

Brinell hardness numbers (3,000-kg load, 10-mm steel ball) were determined 2.54 cm from the top and 5.08 cm from the bottom of each as-cast ingot. As expected, ingot hardness was directly proportional to oxygen, nitrogen, and silicon contents. Harder ingots (BHN range: 174–218

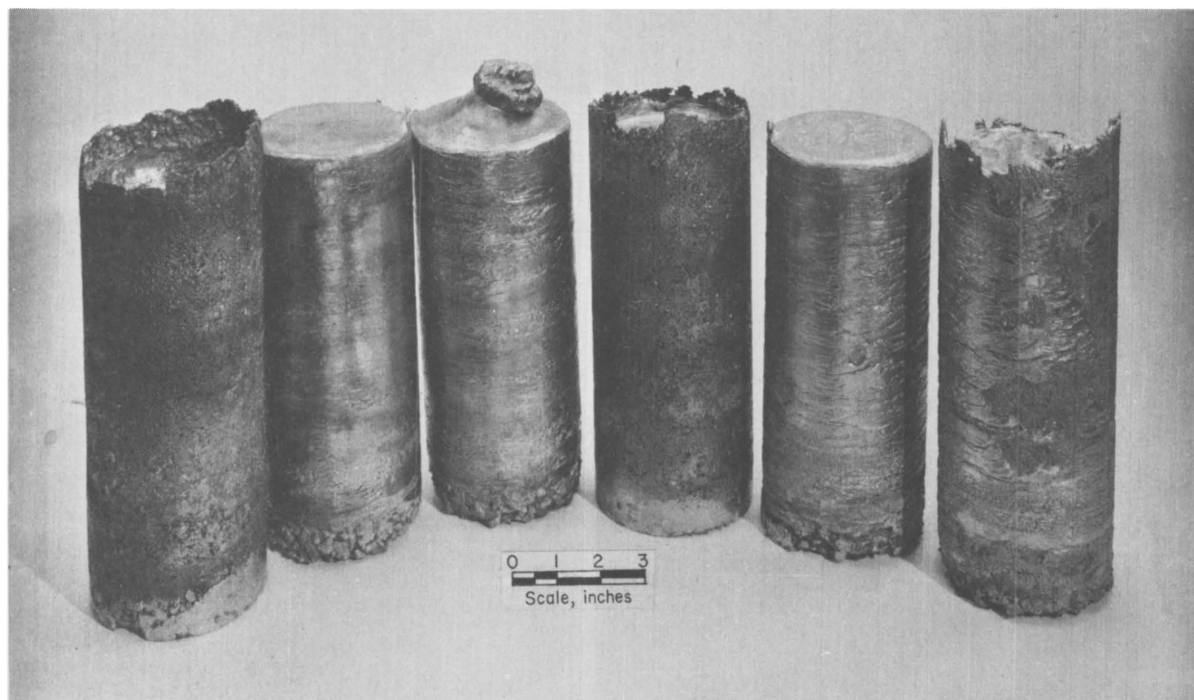


Figure 74.—Complete series of reactor-grade zirconium sponge ingots prepared by vacuum-arc melting and electroslag melting with CaF_2 . The first ingot on the left was vacuum-arc-melted with straight-polarity dc. The second and third ingots from the left were electroslag-melted with straight-polarity dc, using $\frac{1}{3}$ atm helium and a helium-sweep atmosphere, respectively. The fourth ingot from the left was vacuum-arc-melted with reverse-polarity dc. The remaining electroslag-melted ingots were produced with reverse-polarity dc, using $\frac{1}{3}$ atm helium (fifth from left) and a helium-sweep atmosphere (right).

Table 30.—Typical impurity contents ¹ of high-iron sponge electrode material and electroslag-melted zirconium ingots

	Impurity, ppm ²														
	Al	C	Cr	Cu	F	Fe	H	Mg	Mn	Mo	N	O	Pb	Si	Ti
High-iron sponge electrode	<20	53	150	<10	ND	750	14	>1000	100	<10	22	1,288	150	120	<20
Vacuum-arc-melted ingot (SA 26639)	200	149	250	<10	ND	720	8	60	75	<20	137	2,180	100	300	45
Electroslag-melted ingot with CaF_2 flux ^{3,4} (SA 26649)	30	61	150	350	80	685	13	200	70	35	130	2,010	200	200	<20
LaF_3 flux ⁵ (SA 26792)	80	221	250	>290	80	720	17	225	150	110	90	1,360	300	225	<20

ND Not determined.

¹ O by inert gas fusion; H by hot extraction; N by the Kjeldahl method; F by a sensitive electrode method; C by combustion; all others by optical emission spectroscopy.

² B ≤ 0.2 ppm; Sn ≤ 5 ppm; Ca, Cd, Co, Ni < 10 ppm; V < 30 ppm; W < 40 ppm; Zn < 50 ppm. Values given are averages of top and bottom samples except for hydrogen, nitrogen, and oxygen. Top location from 1 to 2 inches (2.5–5 cm) below top of ingot; bottom location from 1 to 2 inches above bottom of ingot.

³ Acid-grade CaF_2 .

⁴ Both electroslag ingots melted under a helium sweep atmosphere and straight polarity dc (consumable electrode negative).



Figure 75.—Electroslag-melted zirconium ingot: High-iron sponge, LaF_3 flux, straight-polarity dc, and a helium-sweep atmosphere at $\frac{1}{3}$ atm total pressure.

top; 173–225 bottom) were obtained from the high-iron sponge than from the reactor-grade material (BHN range: 112–179 top; 144–186 bottom) and evaluation slab electrodes (BHN range: 142–179 top; 147–189 bottom). Hardness values did not correlate with mechanical properties, but material from the harder ingots was found to be less corrosion resistant. Pertinent data will be given later in this chapter.

PREPARATION OF INGOTS FOR EVALUATION

The ingots were machine-conditioned to remove surface defects and subsequently cut laterally into two equal portions. The ingot sections were then heated to 900°C ($1,652^\circ\text{F}$) for 2 hours and press-forged to $\sim 5\text{-cm}$ (2-inch) thick by ~ 8.3 to 8.9-cm ($3\frac{1}{4}$ -inch) wide billets in two or three workings with intermediate reheats. The vacuum-arc-melted material showed very little oxidation, whereas electroslag-melted material from reactor-grade sponge showed excessive oxidation with some cracking at this stage. The resulting forgings were reheated and rolled to 1.9- to 2.3-cm (0.75- to 0.90-inch) thick by 20.3- to 21.6-cm (8- to 8.5-inch) long slabs. The slabs were conditioned by grinding and sandblasting, reheated to 900°C for 30 minutes, and then cross-rolled in three passes to $\sim 1.3\text{-cm}$ ($\frac{1}{2}$ -inch) thick by $\sim 20.3\text{-cm}$ (8-inch) long plate for impact specimens. The remaining plate from the top half of the ingots was reheated to 850°C ($1,562^\circ\text{F}$) for 30 minutes and rolled to 0.64-cm ($\frac{1}{4}$ -inch) thick plate in one to three passes with 10-minute reheats to temperature between workings. The plate was alpha-annealed at 800°C ($1,292^\circ\text{F}$) for 30 minutes and descaled by grit-blasting. The 0-percent cold-rolled material was hot-rolled at 800° to 850°C ($1,472^\circ$ to $1,562^\circ\text{F}$) to $\sim 0.16\text{ cm}$ (0.0652 inch) solution-treated ($\frac{1}{2}$ -hr water quench), reheated 10 minutes, and air-cooled. The remaining material was hot-rolled to adjust thickness, alpha-annealed at 700°C for 1 hour, and subsequently cold-rolled at 10-percent reduction per pass to final reductions of 10 to 50 percent in 10-percent increments, and to a final thickness of $\sim 0.16\text{ cm}$ ($\frac{1}{16}$ inch). This sheet was used for metallographic observations and tensile and corrosion testing.

METALLOGRAPHY AND MICROPROBE RESULTS

Metallographic specimens were taken from each as-cast ingot, mounted, ground, and polished with standard procedures. Metallographic

Table 31.—*Typical impurity levels¹ in evaluation slab electrode metal and electroslag-melted zirconium ingots*

	Impurity, ppm ²														
	Al	C	Cr	Cu	F	Fe	H	Mg	Mn	Mo	N	O	Pb	Si	Sn
Fused-slab electrode ³	30	ND	<25	26	ND	<400	ND	10	<15	<12	50	1,122	30	37	28
Electroslag-melted ingots:															
Fast melt rate (~5.5 lb/min [~2.5 kg/min], SA 26652)	<20	43	150	<13	85	420	9	<10	30	<13	30	1,014	50	<20	<23
Slow melt rate (4.2 lb/min [~1.9 kg/min], SA 26781)	30	41	125	60	35	465	15	<5	40	<10	47	1,191	70	110	23

ND Not determined.

¹ O by inert gas fusion; H by hot extraction; N by the Kjeldahl method; F by a sensitive electrode method; C by combustion; all others by optical emission spectroscopy.² B ≤ 0.2 ppm; Ca, Cd, Co < 10 ppm; Ni ≤ 12 ppm; V < 30 ppm; Ti, W < 40 ppm; Zn < 50 ppm. Values given are averages of top and bottom samples except for hydrogen, nitrogen, and oxygen. Top location from 1 to 2 inches (2.5–5 cm) below top of ingot; bottom location from 1 to 2 inches above bottom of ingot.³ Average of 3 production-grade evaluation ingots.NOTE.—These melts were conducted with acid-grade CaF₂ flux dynamic helium sweep at 1/3 atm total pressure and reverse polarity dc.

specimens (~1.27 cm [1/2 inch] square) were also cut from each 0.16-cm (1/16-inch) thick sheet. Representative photomicrographs are shown in figures 76 and 77.

A basket-weave structure is present in all as-cast ingots, as are small (<5-micrometer) inclusions which possibly contain oxygen, nitrogen,

and/or carbon, and one or more transition metal elements. Distinct grain boundaries outlined by such particles are present in the material electroslag melted with LaF₃. The 0-percent cold-rolled material shows a single ripply phase. Electron microprobe results verify the presence of small, randomly distributed CaF₂ particles in material

Table 32.—*Typical impurity levels¹ in reactor-grade sponge and zirconium ingots melted therefrom*

	Impurity, ppm ²															
	Al	C	Cr	Cu	F	Fe	H	Mg	Mn	Mo	N	Ni	O	Pb	Si	Ti
Reactor-grade sponge electrode ³	ND	23	ND	ND	<20	590	16	ND	ND	ND	14	ND	999	ND	ND	ND
Vacuum-arc-melted ingots:																
SA 26800 ⁴	50	65	250	28	<20	645	12	30	90	60	24	10	904	40	<20	<20
SA 26804 ⁵	<20	68	150	15	<20	685	23	18	30	<15	31	5	903	60	<20	<20
Vacuum-arc remelts:																
SA 26874 ^{5*}	<30	143	135	30		735	9	<5	15	30	29	13	1,190	20	<60	100
SA 26875 ^{4†}	20	82	135	15		665	4	<5	15	30	24	15	1,160	15	90	20
Electroslag-melted ingots:																
SA 26805 ^{5*}	<20	75	80	<10	105	750	36	45	35	155	39	5	935	80	<110	<50
SA 26806 ^{5*}	<20	77	160	25	80	740	34	65	45	365	27	7	957	80	<160	<110

ND Not determined.

¹ O by inert gas fusion; H by hot extraction; N by the Kjeldahl method; F by a sensitive electrode method; C by combustion; all others by optical emission spectroscopy.² B ≤ 0.2 ppm; Sn < 8 ppm; Ca, Cd, Co < 10 ppm; V < 20 ppm; W < 40 ppm; Zn < 50 ppm for all melts except that for SA 26874 B = 6 ppm and Sn ≤ 253 ppm; and for SA 26875 B = 5 ppm and Sn < 28 ppm. Values given are averages of top and bottom samples except for hydrogen, nitrogen, and oxygen. Top location from 1 to 2 inches (2.5–5 cm) below top of ingot; bottom location from 1 to 2 inches above bottom of ingot.³ From melted evaluation button. For impurities for which no values are given, see SA 26800 and SA 26804.⁴ Consumable-electrode dc negative.⁵ Consumable-electrode dc positive.⁶ Remelt of SA 26804.⁷ Remelt of SA 26800.⁸ Acid-grade CaF₂ flux; SA 26805 melted under 1/3 atm static helium; SA 26806 melted under helium sweep at 1/3 atm total pressure.

Table 33.—*Typical impurity contents of fluxes for zirconium electroslag melting*

Melt	Impurity (numerical values reported in ppm)												
	Al	C	Ca	Cu	Fe	Mg	Mn	Mo	N	Si	Ti	Y	Zr
SA 26619: ¹													
Unused	D	441	A+	E	D+	D+	ND	E+	10	D+	B+	ND	D
Used top	D+	97	A+	E+	ND	E+	ND	ND	16	ND	E+	ND	C+
Used sidewall	D+	235	A+	D+	D	D	ND	D+	79	E+	B+	ND	B
SA 26623: ²													
Unused	C+	62	A+	ND	D+	E+	E+	B	12	C	C	ND	ND
Used top	D+	116	A+	ND	ND	B	ND	C	12	ND	—	ND	C+
Used sidewall	D	180	A+	ND	ND	B	ND	C	19	D+	—	ND	B+
SA 26649: ³													
Unused	C+	62	A+	ND	D+	E+	E+	B	12	C	C	ND	ND
Used top	E+	287	A+	ND	ND	D+	ND	ND	29	E+	C	E+	C+
Used sidewall	D+	644	A+	D	D+	B+	ND	C	795	D+	C+	E+	B
SA 26803: ⁴													
Unused ⁵	ND	ND	ND	F	ND	C	ND	ND		ND	C	ND	C+
Used top ⁶	ND	ND	B+	ND	ND	F+	ND	ND		ND	C	ND	ND
Used sidewall ⁷	ND	ND	C	C	C	B	D+	D+		ND	D	ND	B+

A+ = 10 to 100 percent

B+ = 1 to 10 percent

B = 0.5 to 3 percent

C+ = 0.1 to 1 percent

C = 0.03 to 0.3 percent

D+ = 0.01 to 0.1 percent

D = 0.003 to 0.03 percent

E+ = 0.001 to 0.01 percent

E = 0.0003 to 0.003 percent

F+ = 0.0001 to 0.001 percent

F = 0.00003 to 0.0003 percent

ND = Not detected spectrographically.

¹ Acid-grade CaF₂, 1/3 atm static helium straight polarity dc, evaluation slab electrode material.² Same as in footnote 1 except reverse polarity dc and high-iron sponge.³ Electroslag-melted ingot with acid-grade CaF₂ flux. Ingots melted under helium sweep atmosphere with straight polarity dc (consumable electrode negative).⁴ LaF₃, 1/3 atm static helium, reverse polarity dc, high-iron sponge.⁵ 40 to 100 percent LaF₃, 1 to 10 percent unidentified.⁶ 40 to 100 percent LaF₃.⁷ 20 to 60 percent LaF₃, 1 to 10 percent Zr + ZrF₄.

worked from electroslag ingots melted with CaF₂ flux. No such fluoride particles were evident when the metal was melted with LaF₃. The small (<5-micrometer) aforementioned inclusions persisted in all of the worked metal, regardless of melting history or electrode material. The basket-weave structure is absent in the worked material.

TENSILE TESTS

Standard ~1.27-cm (1/2-inch) wide, ~5-cm (2-inch) gage length specimens cut parallel and perpendicular to the rolling direction were prepared from each 1/16-inch sheet described previously. The specimens were tested on a ~27,000-kg (60,000-pound) Baldwin tensile-testing machine at room temperature with a strain rate of 0.005 in/in-min to yield and 0.05 in/in-min to failure. Typical results are summarized in figure 78. Both tensile and yield strengths varied with the type of electrode stock and, for the high-iron sponge, with slag composition and melting technique, for any given percent of cold work reduction. This reflects the variation in oxygen levels in the as-cast ingots (tables 30 and 32). The

percent elongation averages for all melts are indicated in figure 78. All of the determined values agree to within 1-percent elongation of the curve drawn in the figure. The percent of elongation therefore appears independent of the melting parameters for all reductions. Over 80 percent of the tested specimens display irregular flat or shear fracture. The remainder show cup-type fracturing. Except as noted in figure 78, differences in tensile strength, yield strength, and percent elongation between specimens cut parallel to the rolling direction and those cut perpendicular were less than the vertical size of the symbols in the figure. However, yield strength in perpendicularly cut specimens was higher than that in the parallel cut specimens at 0-percent cold-work reduction.

IMPACT TESTS

Coupons 6.35 by 1.27 by 1.27 cm (2 1/2 by 1/2 by 1/2 inch) in size were cut from 1/2-inch-thick rolled plate from the bottom half of each ingot according to the layout shown in figure 79. Charpy V-notch specimens (55 by 10 by 10 mm) were machined from these coupons with equal

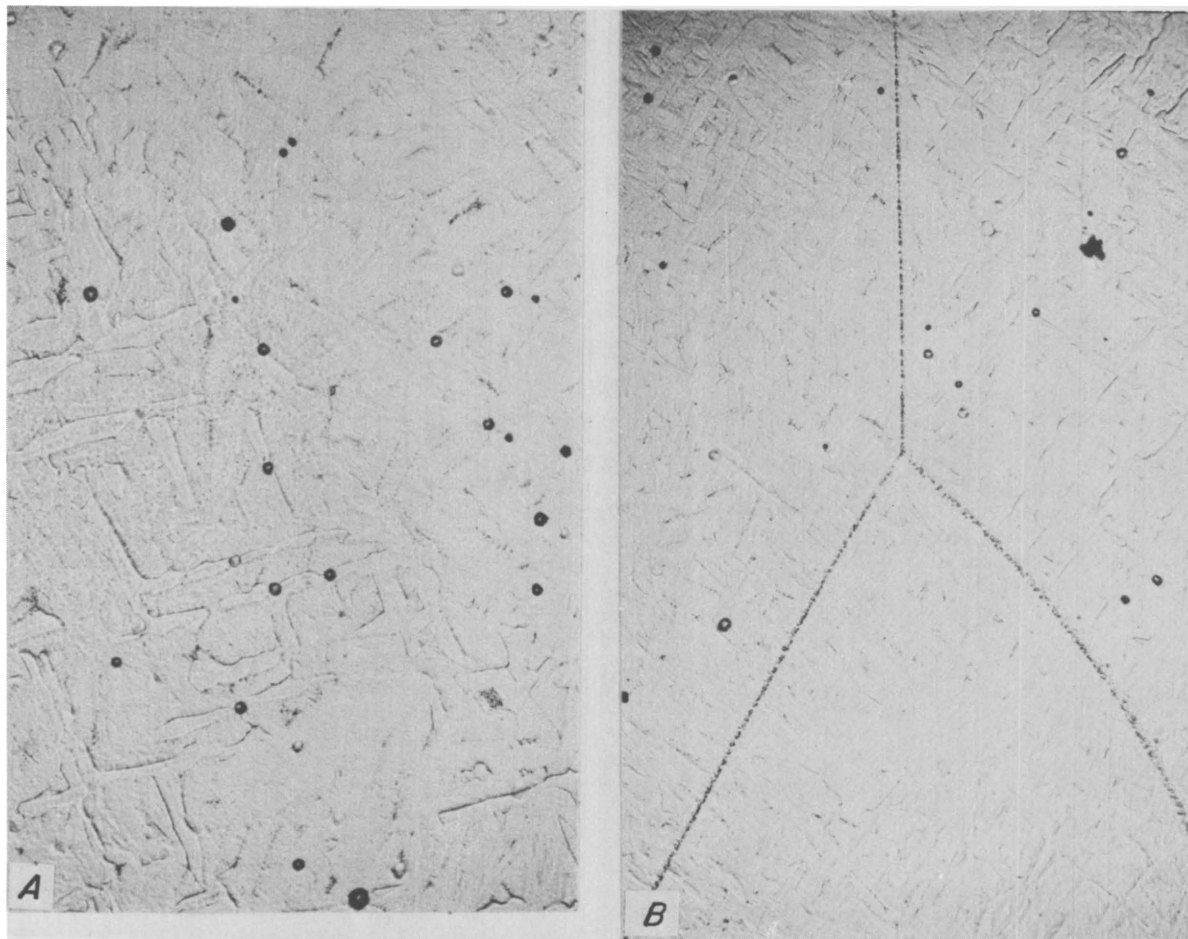


Figure 76.—Zirconium melted from high-iron sponge. *A*, As-cast ingot SA 26649, CaF_2 slag, 250 X, etched with 10 ml HF, HNO_3 45 ml H_2O solution; *B*, as-cast ingot SA 26803, LaF_3 slag, longitudinal section, 150 X, same etchant.

amounts of material removed from each face. The V-notch was 2 mm deep and centered on the top surface. Impact tests on the wrought products were conducted in air at room temperature on a Riehle impact tester with a 0- to 220-ft-lb-capacity range. Representative results are presented in table 34 as a function of melting parameters. All tested specimens exhibited a brittle-type fracture with a silky, fractured surface after testing. Selected fractured impact specimens from coupon 5 were examined by electron microscopy. Failure occurred by cleavage. Some rounded second-phase particles were found on the cleavage faces, and the presence of hydride flakes could not be observed. Impact strength appears to be independent of coupon location in the ingot or the angle to

the longitudinal direction of the ingot. However, coupons from the middle of the ingot (3 and 4) occasionally exhibit greater impact strength than those from other locations (SA 26649, SA 26803, and SA 26875). The coupons from vacuum-arc-remelted ingots showed significantly greater impact strength than those from either vacuum-arc or electroslag first-melted ingots. Little or no difference was observed in impact strengths as a function of the melting parameters studied. No impact strength improvement was noted in electroslag first-melted material over vacuum-arc first-melted zirconium.

CORROSION TESTS

Corrosion coupons ($1\frac{1}{8}$ inches or 2.86 cm square) were cut from each of the ~ 0.16 -cm

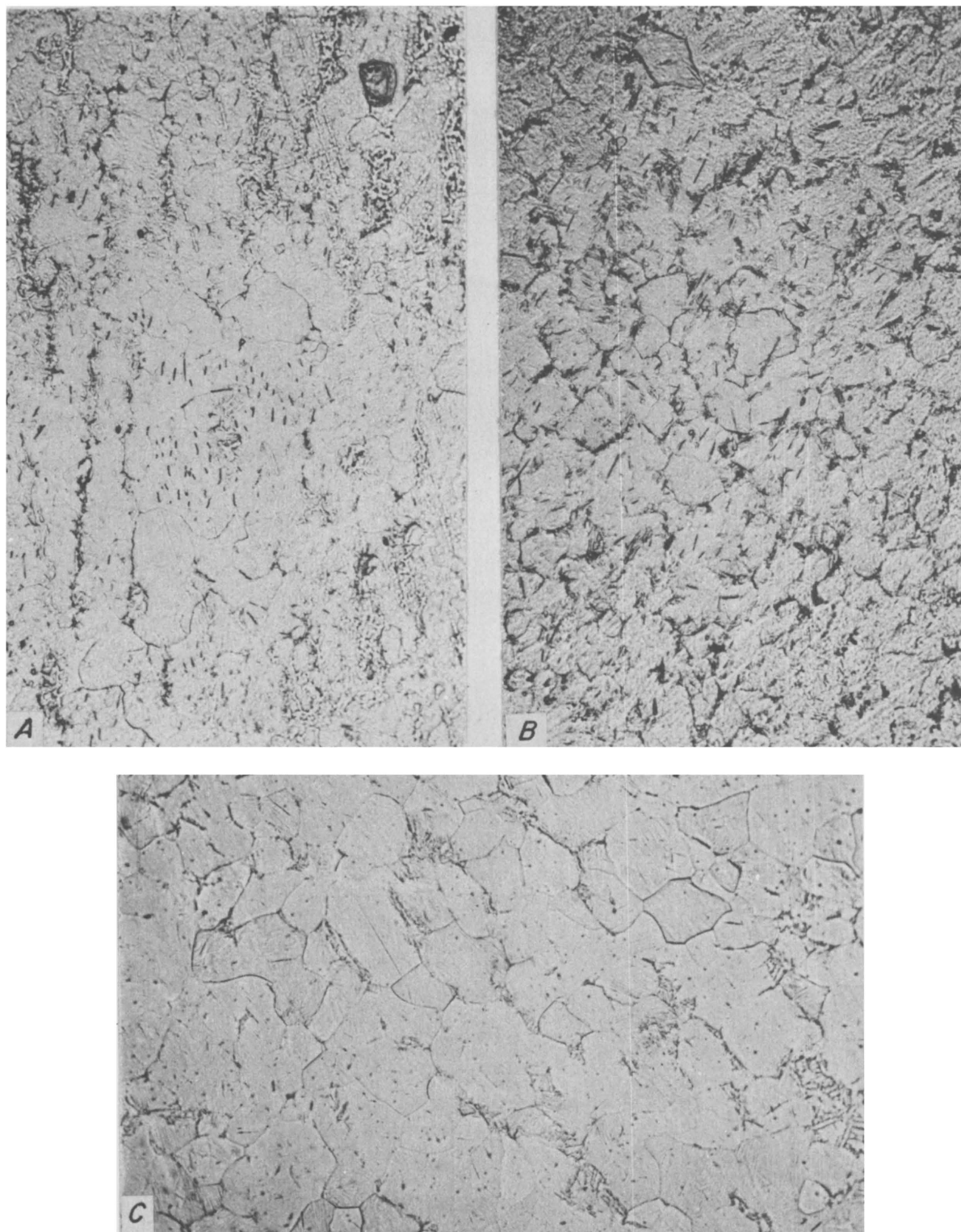


Figure 77.—Zirconium sheet after hot rolling (0 pct cold rolled). *A*, From ingot SA 26649, CaF_2 slag, high-iron sponge, 250 X, same etchant as in figure 76, *B*, from ingot SA 26805, CaF_2 slag, reactor-grade sponge, 250 X, same etchant, *C*, from ingot SA 26875, vacuum-arc-remelted, reactor-grade sponge, 250 X, same etchant.

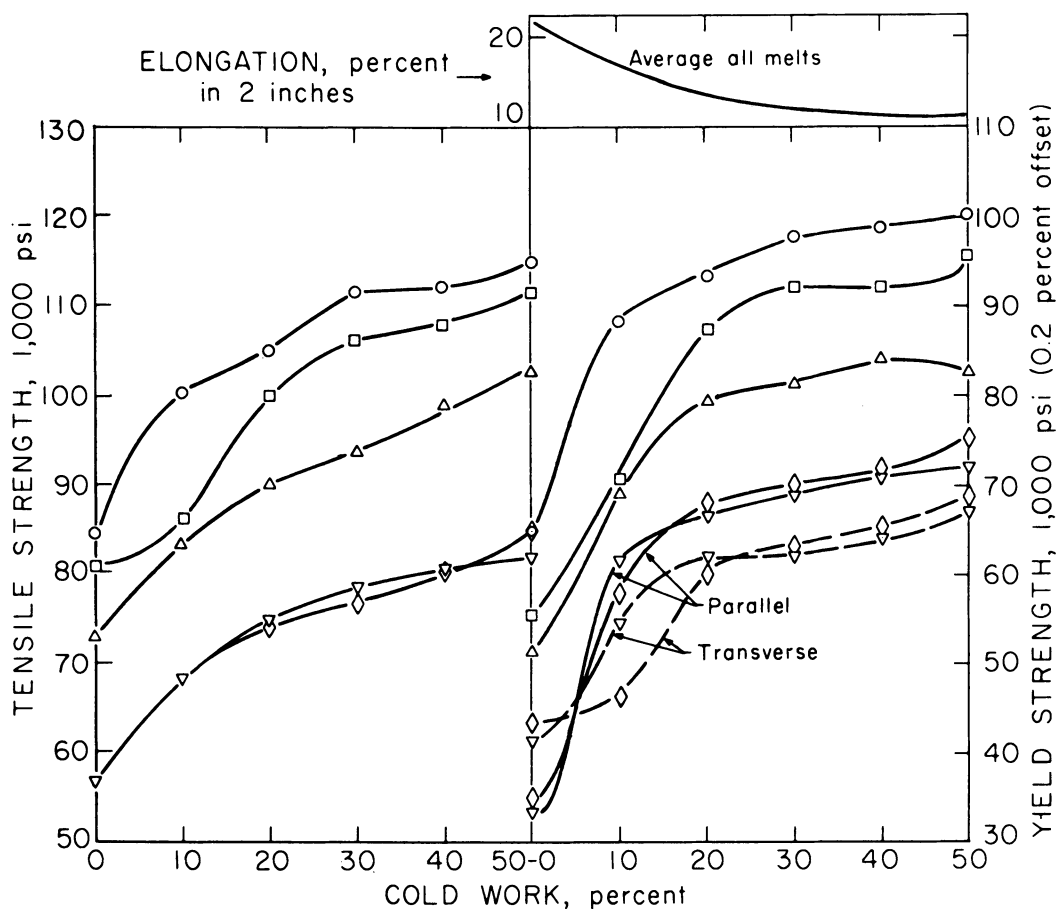


Figure 78.—Tensile properties of vacuum-arc- and electroslag-melted zirconium. All of the curves represent an average of two tests each on transverse and longitudinal specimens, except where noted. Symbols have the following meanings:

- Vacuum-arc-melted high-iron sponge (SA 26639).
- Electroslag-melted (CaF_2) high-iron sponge (SA 26649).
- △—Electroslag-melted (LaF_3) high-iron sponge (SA 26792).
- ◇—Electroslag-melted (CaF_2) reactor-grade sponge (SA 26805).
- ▽—Vacuum-arc-remelted reactor-grade sponge (SA 26875).

($1/16$ -inch) thick sheets described previously. Autoclave tests were conducted in steam (pH = 6.1 to 6.8; resistivity- 10^6 ohm-cm) at 399°C (750°F) and 1,500 psi; and in saturated steam (pH = 6.3 to 6.7; resistivity- 10^6 ohm-cm) at 360°C (680°F) and 2,705 psi. Corrosion tests were interrupted after 5 days, at which time most specimens had formed a black, glossy, tightly adhering oxide, characteristic of zircaloy. Some specimens were

mottled with a white oxide within the black film. The amount appeared inversely proportional to the amount of cold working.

In the vacuum-arc-melted material, a heavy white oxide formed at the coupon edges. Subsequently, all of the coupons except those derived from vacuum-arc-melted and CaF_2 electroslag-melted ingots (high-iron sponge) were subjected to the corrosion media for an additional 9 days,

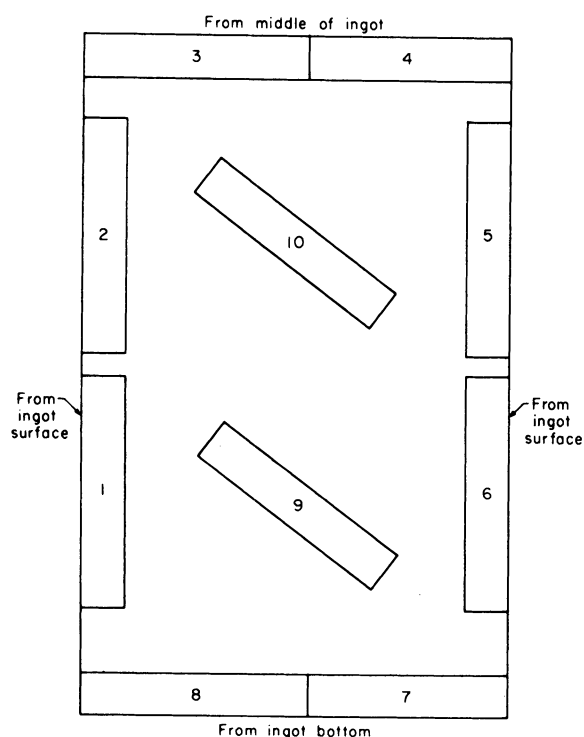


Figure 79.—Layout of 1.27-cm (1/2-inch) plate for cutting coupons from which Charpy V-notch specimens were machined.

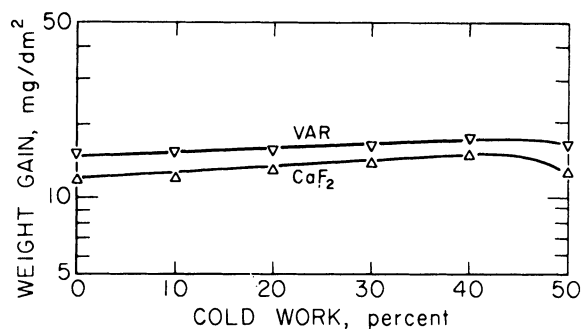


Figure 80.—Weight gain versus percent cold work for electroslag- (CaF_2 ; Δ) and vacuum-arc-remelted (∇) reactor-grade zirconium sponge. Corrosion test medium was saturated steam at 680°F and 2,705 psi, with an exposure time of 14 days. The vertical size of the symbols represents the uncertainty.

giving a total testing time of 14 days. Zircaloy-2 control coupons were present throughout the tests for comparison purposes.

No systematic variation of corrosion resistance as a function of percent cold work was noted in the specimens tested. This is demonstrated in figure 80, which shows a slight increase in weight gain of the coupons with increasing cold work and a slight decrease in the 50-percent cold-

Table 34.—Impact strengths (ft-lb) of plates fabricated from electroslag- and vacuum-arc-melted zirconium ingots

Melt ¹	Coupon number (see fig. 79)										Average ²
	1	2	3	4	5	6	7	8	9	10	
26639 ³	5	5	11	11	11	11	11	11	10	11	9.7 ± 2.4
26875 ⁴	18	17	20	21	17	18.5	18	17	17	18	18.2 ± 1.2
26620 ⁵	6	7	6.5	6	6.5	6.5	6	6	7	(⁶)	$6.4 \pm .4$
26649 ³	(⁶)	10.5	10.5	(⁶)	9	9	7	6	8	8	8.5 ± 1.5
26805 ⁴	7	5.5	(⁶)	5	6	6.5	6	6	7.5	6	$6.2 \pm .7$
26792 ³	7	6.5	7	6.5	7	7	7.5	8	8	7.5	$7.2 \pm .5$
26803 ⁶	8	8	11.5	11	8	8.5	10	10	9.5	9	9.4 ± 1.2

¹ SA 26,639 is a vacuum-arc melt, SA 26,875 is a vacuum-arc remelt, and the remainder are electroslag first melts.

² 1 standard deviation indicated.

³ 26638 was vacuum-arc melted, 26649 was electroslag-melted with acid-grade CaF_2 flux, helium sweep atmosphere, and straight-polarity dc; 26792 was electroslag-melted with LaF_3 flux and same atmosphere and polarity.

⁴ 26875 was vacuum-arc remelt of vacuum-arc-melted ingot, straight-polarity dc; 26805 was electroslag-melted ingot using acid-grade CaF_2 flux and 1/3 atm static helium, dc electrode polarity positive.

⁵ High-iron sponge electrode; acid-grade CaF_2 flux; straight dc polarity; 1/3 atm helium.

⁶ Material failed.

⁷ Electroslag-melted ingot using LaF_3 flux, 1/3 atm static helium, reverse polarity dc, high-iron sponge.

worked material. In the absence of a statistical analysis to separate the effects of single ingot impurities (such as Al, Mn, Si, O, and N), it is difficult to significantly correlate corrosion resistance with impurity levels. However, observed weight gains appear to be directly proportional to the aforementioned impurity levels (compare figures 81 and 82 with tables 30 and 32). Melting parameters such as polarity and furnace atmosphere exert no apparent influence on corrosion resistance of the wrought shapes. The effect of exposure time in both test media is shown in figure 81. The curves are drawn as straight lines to show the relative corrosion resistance as a function of operational parameters, although actual linearity is not implied. Zirconium melted from high-iron sponge shows significantly greater weight gains than that melted from reactor-grade sponge in both test media. Material electroslag melted with CaF_2 and vacuum-arc-remelted material are similar in corrosion resistance, especially with longer exposure to the test media. In the electroslag-melted metal, slightly greater weight gains are indicated when LaF_3 fluxes were used instead of CaF_2 . All of the wrought material tested shows greater weight gains than arc-melted crystal bar zirconium (3). The same trends are indicated as a function of temperature, although the differences between electrode stock are not as apparent. This is shown in figure 82 from 0-percent and 20-percent cold-worked material. Material melted from high-iron sponge (vacuum-arc first-melt) was more susceptible to oxidation in both media after 5 days' exposure than other material (electroslag or reactor-grade sponge). The same was true for CaF_2 electroslag-melted high-iron zirconium tested in saturated steam.

CONCLUSIONS

Satisfactory 10-cm (4-inch) diameter zirconium ingots have been produced from three different sources by the electroslag process with dc power. On the basis of this work, electroslag melting of zirconium offers the same potential advantages and suffers identical shortcomings as it does when used to melt titanium. (See chapters 7, 8,

and 9.) Regardless of variations in operating parameters, minimal changes in chemistry can be expected from electrode to ingot as a result of applying this process to zirconium. This method may, therefore, offer a suitable means whereby small quantities of desirable elements can be retained throughout the melting process. Alternate methods such as vacuum-arc melting to reduce impurities prior to electroslag melting are a prerequisite if these impurities must be minimized in the as-cast ingot. Oxygen, nitrogen, and silicon, as well as possibly one or more transition elements, are also responsible for small observed inclusions. Flux composition plays a role in this respect since less stable fluxes (such as CaF_2) were found in the ingots as discrete particles, whereas this is not the case when fluxes with greater high-temperature stabilities (for example, LaF_3) are used.

Mechanical properties such as tensile strength and yield strength, as well as corrosion resistance, are chiefly a function of electrode stock which reflects differences in electrode impurity levels. On the other hand, percent elongation and impact strength appear independent of all melting parameters. Impact strength is greater in vacuum-arc-remelted zirconium than in either electroslag or vacuum-arc first-melted material. Corrosion resistance appears similar in electroslag- and vacuum-arc-melted and could not be definitely correlated with melting parameters or percent cold work of the wrought shapes.

It has also been observed that inclusions play an important role in grain growth and transformation. Electroslag-melted zirconium also exhibited a large increase in high-temperature (500°C) creep strength over conventionally melted material, according to A Mitchell, University of British Columbia (1974).

ACKNOWLEDGMENTS

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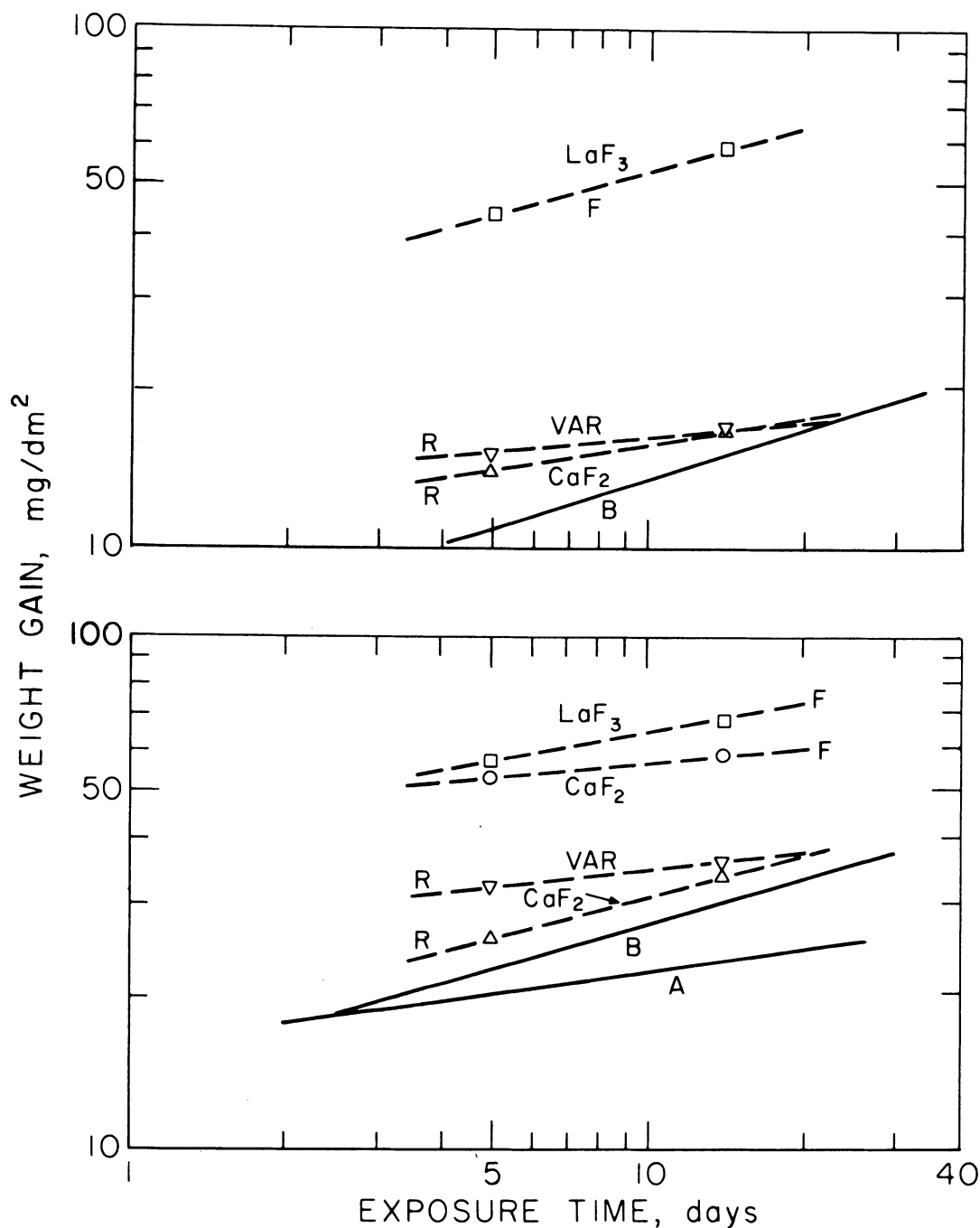


Figure 81.—Weight gain as a function of exposure time for electroslag- and vacuum-arc-melted 40 percent cold-worked zirconium. Solid curves represent corrosion data for arc-melted zirconium sponge (A) and crystal-bar zirconium (B) (3). Conditions for top panel were saturated steam at 680° F and 2,705 psi; conditions for bottom panel were steam at 750° F, and 1,500 psi. Symbols have the following meanings:

- Electroslag-melted high-iron (F) sponge (CaF₂ flux, average of three ingots).
- Electroslag-melted high-iron (F) sponge (LaF₃ flux, average of two ingots).
- △—Electroslag-melted reactor-grade (R) sponge (CaF₂ flux, average of two ingots).
- ▽—Vacuum-arc-remelted reactor-grade (R) sponge (average of two ingots). The vertical separation of the symbols represents the uncertainty.

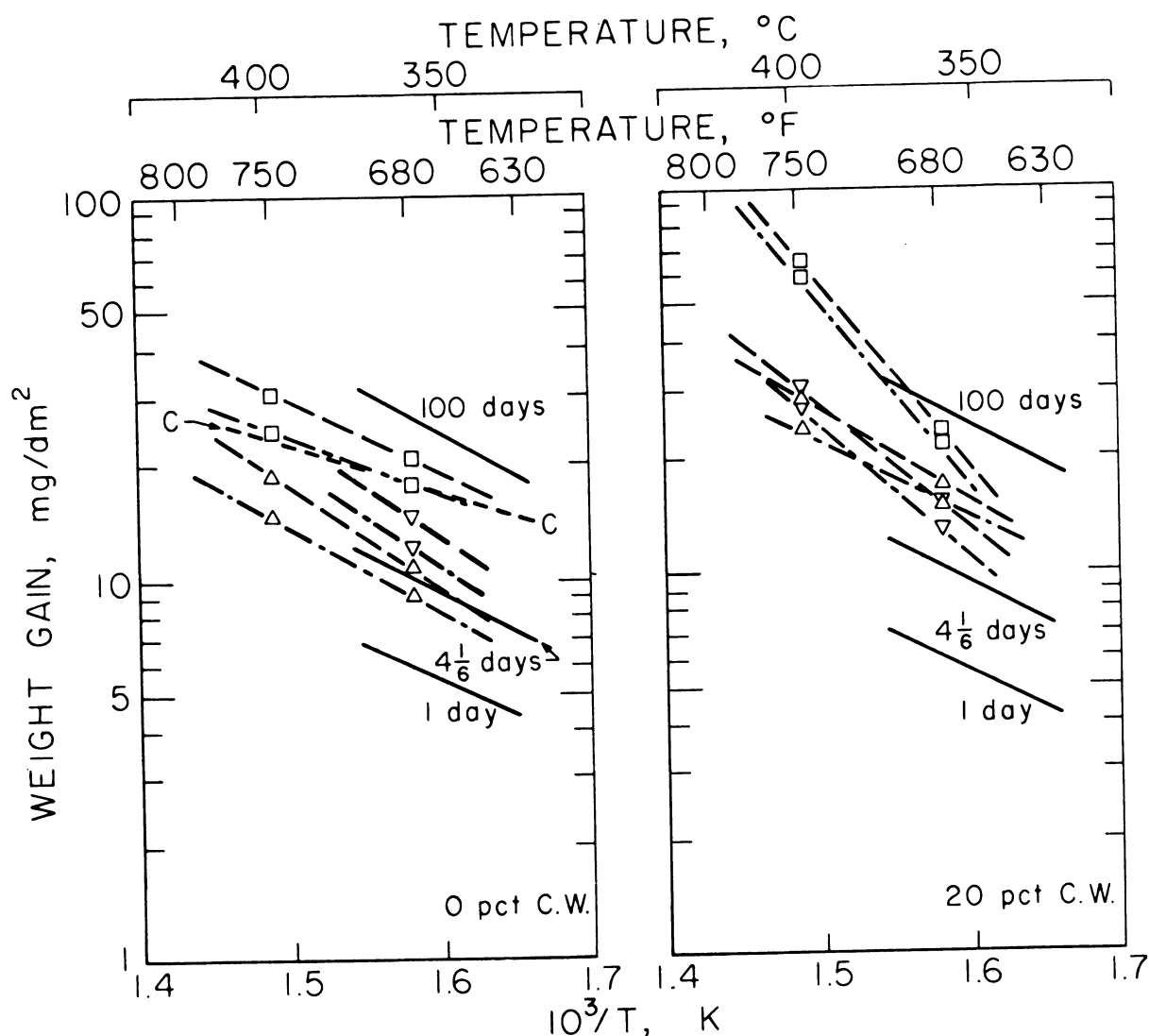


Figure 82.—Effect of temperature on weight gain for electroslag and vacuum-arc-melted 0-percent (left) and 20-percent (right) cold-worked zirconium. Solid curves indicate corrosion data for crystal bar zirconium in water (3). Dot-dashed curves are data for 5 days' exposure time; dashed curves represent 14-day exposures. Curve C represents data for Zircaloy -2 control coupons.

□—Electroslag-melted high-iron sponge (LaF_3 flux, average of three ingots).
 △—Electroslag-melted reactor-grade sponge (CaF_2 flux, average of two ingots).
 ▽—Vacuum-arc-remelted reactor-grade sponge (average of two ingots). The vertical separation of the symbols represents the uncertainty.

CHAPTER 11.—ELECTROSLAG REMELTING OF COPPER AND ITS ALLOYS

By R. H. Nafziger

A major problem in melting copper is the removal of oxygen from the metal. Oxygen is detrimental because it forms cuprous oxide which produces a grain-boundary eutectic with the copper (6). This lowers the plasticity and corrosion properties of the metal and limits successful cladding, tinning, and soldering. In addition, oxygen contamination makes copper susceptible to hydrogen embrittlement. Commercial oxygen-free copper is produced by complex and expensive means. Interest is therefore widespread in developing a simple and inexpensive technique for preparing this type of copper. One possible approach involved the electroslag process with its potential for refinement by the flux and demonstrated capability for independent adjustment of a wide variety of melting parameters. A brief pioneering investigation was conducted at the Albany Metallurgy Research Center by the author to gain sufficient information to guide future research planning. The results of this otherwise unreported research are presented herein.

EXPERIMENTAL WORK

Sections of copper pipe 3.2 cm in OD by 1.6 cm in ID served as the electrode material in a series of 7.6-cm-diameter straight-polarity dc melts. Each section was 30 to 33 cm in length. The furnace and auxiliary equipment were similar to that described in chapter 7. All of the melts were conducted in a furnace which had been evacuated to 3 to 5 x 10⁻² torr and subsequently backfilled to 1/3 atm helium prior to melting. Nominal power was 1,100 to 1,400 amperes at 14 to 25 volts. Table 35 illustrates the melting parameters used. The fluxes were fused in accordance with the procedures outlined in chapter 7.

RESULTS

Ingots characterized by an absence of porosity and inclusions but with relatively rough surfaces

Table 35.—*Melting parameters for electroslag copper melts*

Melt	Melt rate, kg min ⁻¹	Power, kw	Kwhr	Energy consump- tion kwhr kg ⁻¹
SA 28889	0.64	42	2.59	1.10
SA 28890	(¹)	38.5	(¹)	(¹)
SA 28892	.47	28	2.33	.99
SA 28893	.74	28	1.45	.63
SA 28894	.89	24	1.12	.49
SA 28895	1.71	56	1.30	.54

¹ Recorder malfunctioned; no data.

were obtained. Smaller amounts of flux and a lower melting rate improved ingot surfaces. Analyses of major impurities are given in table 36. From this table, the following observations are noted: (1) Ingot carbon is minimized by NaCl and NaF additions to the flux, (2) the molten metal absorbs calcium from the flux except when a MgF₂-CaF₂ eutectic composition is used, (3) all fluxes pick up some copper from the metal (this is minimized with carbon and NaCl additions to the flux), and (4) ingot oxygen is minimized when NaCl, NaF, and carbon are added to the flux in separate melts; alkaline-earth fluoride fluxes alone are not satisfactory for reducing ingot oxygen. It is therefore recommended that a deoxidant be added to the flux and that carbon should be added in the form of a compound (such as CaC₂) rather than as graphite, to prevent fuming and carbon separation on the flux and ingot surfaces. Further deoxidation may be achieved by ac melting.

COPPER ELECTROSLAG REMELTING IN THE SOVIET UNION AND WEST GERMANY

Russian investigators have published results on electroslag remelting of copper. Pogodin-Alekseev and Syrovatkin (6) used cathode copper

Table 36.—Results of electroslag melting unalloyed copper

	Major impurities, ppm (unless otherwise indicated)									Ingot	
	Ba	C	Ca	Cu	H	Mg	N	Na	O	Grain size and orientation	Metal- lography
SA 28889: 49 WT-PCT MgF ₂ -51 WT-PCT CaF ₂ (EUTECTIC) , 700 GRAMS											
Electrode	ND	<10	ND	Major	1	ND	<5	ND	31	2.54 cm Radial (deep pool)	1 phase.
Ingot	ND	61	ND	Major	1	0.3-3 pct	<5	ND	471		
Unused slag ...	279	91	Major	ND	NA	Major	12	ND	NA		
Used slag	2,786	285	Major	1-10 pct	NA	Major	11	ND	NA		
SA 28890: 49 WT-PCT MgF ₂ -51 WT-PCT CaF ₂ (EUTECTIC) , 350 GRAMS											
Electrode	ND	57	ND	Major	2	ND	<5	ND	53	Elongate (shallow pool)	1 phase.
Ingot	ND	76	ND	Major	2	0.3-3 pct	<5	ND	306		
Unused slag ...	ND	91	Major	ND	NA	Major	12	ND	NA		
Used slag	86-857	230	Major	1-10 pct	NA	Major	<5	ND	NA		
SA 28892: 75 WT-PCT BaF ₂ -25 WT-PCT CaF ₂ , 340 GRAMS											
Electrode	ND	16	ND	Major	1	ND	<5	ND	35	1.00 cm Radial (shallow pool)	1 phase plus grain-boundary phase.
Ingot	ND	171	300- 3,000	Major	3	ND	<5	ND	151		
Unused slag ...	Major	89	Major	ND	NA	1-10	14	300- 3,000	NA		
Used slag	Major	86	Major	1-10 pct	NA	0.003- 0.03 pct	10	ND	NA		
SA 28893: 71.4 WT-PCT BaF ₂ -23.8 WT-PCT CaF ₂ -4.8 C, 450 GRAMS											
Electrode	ND	<10	ND	Major	1	ND	<5	ND	31	Axial	1 phase plus grain-boundary phase.
Ingot	ND	269	300- 3,000	Major	3	ND	<5	ND	49		
Unused slag ...	Major	ND	Major	ND	NA	0.023- 0.23 pct	ND	ND	NA		
Used slag	Major	5.35 pct	Major	2.3-23	NA	ND	6	ND	NA		
SA 28894: 10 WT-PCT NaCl-90 WT-PCT CaF ₂ , 450 GRAMS											
Electrode	ND	57	ND	Major	2	ND	<5	ND	53	Axial	1 phase
Ingot	ND	38	100- 1,000	Major	1	3-30	<5	ND	53		
Unused slag ...	ND	191	Major	ND	NA	3-30	15	0.3-3 pct	NA		
Used slag	ND	458	Major	3.7-37	NA	0.0093- 0.093 pct	11	1-10 pct	NA		
SA 28895: 17 WT-PCT NaF-83 WT-PCT CaF ₂ , 450 GRAMS											
Electrode	ND	16	..	Major	1	ND	<5	ND	35	Axial	1 phase
Ingot	ND	14	30- 300	Major	2	1-10	5	ND	48		
Unused slag ...	ND	137	Major	ND	NA	3-30	13	1-10 pct	NA		
Used slag	67- 667	<20	Major	1-10 pct	NA	0.078- 0.78 pct	<5	1-10 pct	NA		

NA Not applicable. ND Not detected.

plates to prepare 50- by 120- by 250-mm rectangular inclusion- and pore-free ingots with a chemically pure fluorspar flux to which unspecified additions were made, presumably to reduce the liquidus temperature. The ingot macrostructure was characterized by equiaxial grains. Tensile, yield, and impact strengths were comparable to those of conventionally cast copper ingots. Chemistry was unchanged from electrode to ingot as a result of the electroslag remelting. Cupric oxide was shown to form at the electrode-flux interface. This was transformed to cuprous oxide in the molten flux bath. The flux then absorbed this oxide and prevented it from forming in the metal. In another study designed to reduce oxygen in electroslag-remelted copper, Latash and Medovar (2) showed that graphite and CaC_2 additions to 80 percent CaF_2 -20 percent BaCl_2 fluxes reduced oxygen in the metal, whereas the halide fluxes alone produced an increase in ingot oxygen. These investigators also noted that calcium carbide was more uniformly dispersed throughout the molten flux than was graphite. However, ingot hydrogen was slightly higher when calcium carbide was employed. Experiments were also conducted under an argon atmosphere with CaF_2 - BaCl_2 and CaF_2 - NaF fluxes. In low-oxygen copper, both a protective atmosphere and a deoxidant are essential in preventing increase in ingot oxygen.

Nearly identical results have been obtained by West German investigators (8).

ELECTROSLAG REMELTING OF BRONZES

Conventional induction melting of chromium bronze has shown that oxidation and chromium

losses reduce yields and cause deterioration of the physical and mechanical properties of the alloy. Soviet investigators (3) have therefore turned to the electroslag process to alleviate these problems. Copper rods or bars with a copper-chromium master alloy (3 to 4 percent chromium) were used as electrodes to melt 80- to 120-mm-diameter ingots with CaF_2 - NaCl (2.5 to 10 percent) fluxes. Chromium losses and metal oxidation were minimized when an inert argon atmosphere was used (7). Uniform grain size, absence of defects and inclusions, a smooth surface, and a two-phase microstructure characterized the ingots. Improved hot workability and weldability were noted for electroslag-remelted material. Mozhaev and coworkers (4-5) have successfully electroslag-remelted chromium bronze with an 80 percent CaF_2 -20 percent BaCl_2 flux and obtained homogeneous, porosity-free ingots with columnar grains. Effective removal of non-metallic inclusions was also observed.

Korenyuk and Didkovskii (1) have ac electroslag-remelted tin phosphorus bronze from plate electrodes into water-cooled copper crucibles. Plate ingots ranged up to 210 by 30 mm in cross section. Best results were obtained with 75 percent CaF_2 -25 percent NaF fluxes. The quality of the ingots was reported to be better than that obtained by semicontinuous-casting techniques.

CONCLUSIONS

The electroslag process offers a possible alternative to conventional melting methods for copper and its alloys. It is recommended that multi-component halide fluxes be used, together with a deoxidant in the flux to minimize oxygen in the metal.

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¹ Titles enclosed in parentheses are translations from the language in which the item was published.

CHAPTER 12.—ELECTROSLAG MELTING OF IRON AND STEEL

By R. H. Nafziger, R. L. Lincoln,¹ J. T. Dunham,² and C. E. Armantrout³

Perhaps the most widely used and accepted application of the electroslag process is in the secondary refining of ferrous alloys. This is reflected in the majority of electroslag publications from many countries.

This chapter presents an overall picture of the electroslag process as it applies to the remelting of specialty steels such as high-speed steels, hot work steels, cold work steels, spring steels, and bearing steels. The emphasis is placed on noted property improvements. Comments are also included concerning electroslag melting experiences on iron and plain carbon steels. In addition, the results of electroslag melting scrap steel at the Bureau of Mines Albany Metallurgy Research are summarized.

The chapter covers all types of steels and iron except stainless steels, which are treated in chapter 13.

IRON

The electroslag process for melting pure iron has application in the production of large magnets. In addition, a few laboratory results have been reported. Williams (36) noted a reduction in oxygen, phosphorus, and silicon in 10-cm-diameter iron ingots electroslag melted with CaF_2 and 80 CaF_2 -20 CaO slags. Phosphorus is more easily removed than sulfur in iron owing to the relatively high initial oxygen content and the low activity of sulfur. Soviet investigators (31) have also noted a decrease in oxygen during electroslag melting of Armco iron. Williams obtained typical electroslag macrostructures and reductions in inclusions. A flux containing less than 10 percent iron oxide and/or with a high viscosity measurably slowed the refining process. However, excessively low molten flux viscosities

such as are found in fluoride slag systems result in a noncontinuous flux skin which causes current shorting, melt instability, and poor ingot surfaces when high current densities are used in attempts to provide cylindrical molten pools (3).

In the past few years, interest has been generated in the electroslag melting of sponge iron. Thomas (35) reported a scheme wherein non-consumable graphite or water-cooled copper electrodes in a three-phase ac furnace were used. Three electrodes were employed in a prototype installation. The sponge iron was fed into the furnace to produce smooth, homogeneous 700-kg ingots using CaF_2 - CaO - Al_2O_3 fluxes. Such a potentially versatile technique would be particularly attractive to small-scale production plants operating at low costs. This is the subject of present research at the Albany Metallurgy Research Center, beginning with prereduced iron ore pellets. However, results are too premature for reporting at this time.

PLAIN CARBON STEEL

In a period of several years, ESRT in Great Britain (see chapter 1) has conducted numerous electroslag experiments with mild steel in an effort to optimize melting parameters, while acknowledging that the commercial electroslag melting of plain carbon steels is unlikely. Sound, high-yield, axially crystallized ingots with smooth surfaces were obtained using a 50 CaF_2 -20 CaO -30 Al_2O_3 flux. Decreases in oxygen and sulfur were noted with an accompanying reduction and dispersion of nonmetallic inclusions (16).

Investigators at the British Electricity Council Research Center at Capenhurst announced several years ago their intention of preparing mild steel slab ingots by the electroslag process, using prereduced iron ore feed material (26). A molten flux start was proposed. It was hoped to melt without excessive losses, retain oxide gangue in the flux, reduce iron oxide to iron, and add alloying additions to obtain mild steel qualities.

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³ Supervisory metallurgist, Albany Metallurgy Research Center (now retired).

No further word on this has been announced, however.

The ESRT group has also experimented with remelting steel and found reductions in Al, B, S, Ti, and Zr in electroslag-melted ingots. Inclusions were decreased and dispersed when a $70\text{CaF}_2\text{--}30\text{Al}_2\text{O}_3$ flux was used. Ingots were sound and possessed smooth surfaces (16).

ALLOY STEELS

If proper consideration is given to melting parameters and slag compositions, a wide range of low- and high-alloy steels can be effectively remelted by the electroslag process. Improvements that have been noted in electroslag-remelted metal over conventionally melted alloy steels include (1) lower sulfur contents, (2) fewer and more uniformly dispersed nonmetallic inclusions, (3) smoother ingot surfaces, (4) greater ingot yield, (5) lower mechanical property anisotropy, and (6) greater homogeneity (16). Results of electroslag melting a limited number of low-alloy and structural steels are given in table 37. For alloy steels, electroslag melting appears to reduce ingot oxygen and sulfur. Some reduction in silicon is also noted, depending on the flux composition used. A 29-percent reduction in oxygen (from 72 to 51 ppm) as a result of electroslag melting structural steels was also experienced by the Japanese when using Al_2O_3 -containing fluxes (17). Nitrogen and hydrogen are evidently unaffected by electroslag melting these steels.

Significant reductions in size and quantity of nonmetallic inclusions have been demonstrated for electroslag-melted alloy and structural steels

(1, 21). In one case, this, together with a reduction in sulfur (0.016 to 0.005 weight-percent), resulted in a marked reduction in anisotropy of impact strengths in structural steels (4). Absolute values of impact strengths were also increased by $\sim 60 \text{ N} \cdot \text{m}$ as a result of electroslag melting (2, 21). Improvements in other mechanical properties such as tensile strength, ductility, rupture strength, and fatigue resistance have been noted in electroslag-melted alloy and structural steels over conventionally air-melted material (1, 7, 28).

An interesting comparison of secondary melting techniques (vacuum induction, vacuum arc, electroslag) with electric furnace melting of chrome-nickel structural steels showed that forged material that had been subjected to secondary melting was less susceptible to the development of cracks. Therefore the effective strengths of such steel were increased (5).

TOOL STEELS

Tool steels were among the first to be electroslag-remelted. As early as 1948, Hopkins (15) reported that great quantities of high-speed steels had been remelted by the electroslag process. In this section, high-speed steels, hot work steels, and cold work steels are considered. There is no justification to electroslag-remelt most shock-resisting and low-alloy tool steels. Satisfactory structures and carbon control are prime considerations in remelted ingots. Typical tool steel fluxes have compositions in the $\text{CaF}_2\text{--CaO--Al}_2\text{O}_3$ or $\text{CaF}_2\text{--CaO--MgO--Al}_2\text{O}_3$ systems (chapter 6). Suitable flux compositions permit reductions in sulfur, oxygen, and sometimes silicon.

Table 37.—Results of electroslag melting alloy and structural steels

Steel and Material	Impurities, wt-pct											Reference
	C	Si	S	P	Mn	Al	Cr	Mo	Ni	O	W	
AISI 4340:												
Electrode ...	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.005	ND	28
ESR ingot ..	ND	ND	ND	ND	ND	ND	ND	ND	ND	.002	ND	
38KhMYuA: ¹												
Electrode ...	0.40	0.36	.007	0.014	0.46	0.78	1.51	0.21	ND	ND	ND	23
ESR ingot ..	.41	.38	.004	.013	.46	.70	1.52	.21	ND	ND	ND	
Soviet structural steel:												
Electrode ...	.35	.28	.020	.015	.75	ND	.90	.36	2.92	.001	ND	21
ESR ingot ..	.36	.17	.010	.013	.75	ND	.87	.35	2.93	.001	ND	

ND Not determined.

¹ Soviet designation.

High-Speed Steels

A recent review (30) of electroslag-remelted high-speed steels has shown superior chemical homogeneity and structural uniformity throughout the ingots, compared with conventionally melted material. The uniform distribution and size of carbides in small ingots is evidently not affected by the power mode. In large-diameter ingots, there is a tendency toward carbide grain growth which probably contributes to the marginal improvement noted in electroslag-remelted ingots over conventionally melted material. Petman, Khvorinov, and Engst (27) have suggested that for optimum high solidification rates, electroslag-remelted high-speed steel ingots should be limited to less than 35 cm in diameter. Inclusion frequencies were notably higher in electroslag-remelted 30- to 40-cm diameter ingots of M1, M2, and M7 varieties than in vacuum-arc-remelted material of equivalent dimensions (30). Electroslag remelting has also extended the drill life of M2 high-speed steels from an average of 75 holes drilled per bit in En9 (0.55 C, 0.85 Mn, 0.1 Cr) material for air-melted material to 90 for electroslag-remelted steel, based on extensive experiments conducted by Osborn Steels (19). In addition, Kirk (19) noted improvements in impact properties of electroslag-remelted T1 high-speed steel over those of conventionally air-melted materials. For example, a 50-percent improvement was obtained at Brinell hardness levels of approximately 600.

With regard to operating parameters during electroslag remelting of high-speed steels, a lower current appears to favor the formation of fewer and smaller carbide colonies, as well as greater reduction in ingot sulfur and manganese (16). Chemical refining, however, is considered of secondary importance in remelting high-speed steels.

Hot Work Steels

It is generally recognized that secondary remelting (by either the electroslag or vacuum-arc process) improves ingot cleanliness and selected mechanical properties over those of conventionally air-melted material. In 5-percent chromium varieties, electroslag remelting gives better yield than vacuum-arc remelting. Otherwise, the two remelting processes produce equal-quality metal with respect to the aforementioned parameters (30). In addition, only minor changes in chemistry (slight reductions in S, Si, and Mn) have been noted as a result of electroslag remelting H-series hot work steels (17,30,33). Care must be

exercised during the melting operations to avoid increases in hydrogen which can cause flaking in these steels.

Table 38 gives some representative examples of mechanical properties of wrought material from electroslag, electric-arc-furnace, and air-melted H11 and H13 hot work steels (13-14, 20, 25). It is evident that electroslag remelting improves tensile strengths, transverse ductility, and impact properties, while anisotropy of these properties is reduced. These improvements can be attributed to improved cleanliness and microstructure with less alloy segregation in electroslag-remelted material (14).

It has been reported (25) that electroslag-remelted H13 averaged 103 MN/m² (15,000 psi) greater fatigue strength (1,103 MN/m² versus 1,000 MN/m²) than air-melted H13 on specimens which were cyclically stressed along the longitudinal axis for 10 million cycles. Another study demonstrated that electroslag-remelted H13 withstood nearly four times as many thermal cycles before crack initiation than did air-melted H13 (25).

Cold Work Steel

Electroslag remelting of cold work steels has been concentrated on the AISI D series. Increased yields have been noted in electroslag-remelted material, provided sufficient attention is paid to stripping practices in order to avoid cracking due to the sensitivity of thermal handling. Aside from sulfur reductions, ingot chemistry during electroslag remelting is essentially unchanged (17). To insure consistent hardenability, the carbon content must be held within narrow limits, which poses no problem in electroslag remelting.

Carbide structures, which are important for wear resistance and strength, show great uniformity and homogenous distribution in electroslag-remelted D2 ingots (30). Grain sizes are often more angular and larger than in conventionally static cast material (18,30).

Improvements in macro- and micro-cleanliness over air-melted wrought material have also been noted in electroslag-remelted D2 (17,30). Worst field ratings for thin globular oxides decreased from 2 to 1½, while heavy inclusions decreased from 1½ to ½.⁴ Similar reductions were noted in sulfide and alumina inclusions (29). Electroslag-remelted A8 cold work steel showed comparable reductions in nonmetallic inclusions.

⁴ ASTM E 45-63 ratings.

Table 38.—Comparison of selected mechanical properties of electroslag-remelted hot work steels with conventionally melted material

Material	Yield strength ¹ MN/m ²		Tensile strength ¹ MN/m ²		Elongation, percent			Reduction, in area, percent			Impact strength, Nm/cm (except as indicated)		
	Long.	Transv.	Long.	Transv.	Long.	Transv.	T/L ²	Long.	Transv.	T/L ²	Long.	Transv.	T/L ²
H11 STEEL													
Air melted: ³													
Edge	NA	NA	NA	NA	13	8	0.6	51	25	0.5	108	69	0.7
Center	NA	NA	NA	NA	12	7	.6	47	17	.3	98	49	.5
Arc-furnace melted ⁴ ...	1,422	1,382	1,559	1,510	14	4	.3	39	8	.2	NA	NA	NA
Electroslag remelted ⁴ ...	1,569	1,539	1,657	1,637	11	11	1.0	39	35	.9	⁵ 137	⁵ 108	.8
H13 STEEL⁵													
Air melted													
(midradius):													
21°C (70°F)	1,424		1,659		5		NA		10	NA		4 ft-lb	NA
482°C (900°F)	1,045		1,258		10		NA		33	NA		NA	NA
Electroslag remelted													
(midradius):													
21°C (70°F)	1,430		1,658		8		NA		24	NA		5 ft-lb	NA
482°C (900°F)	1,066		1,270		13		NA		41	NA		NA	NA

NA Not available.

¹ To convert to approximate psi, multiply by 145; MN is a meganewton, or 10⁶ newtons in the metric system.² T/L is transverse to longitudinal ratio (a measure of isotropy).³ Ingots were 500 mm square, with a subsequent forging ratio of 5:1 (20).⁴ Averages of edge, midradius, and center location of numerous ingots melted over a 2-year period. Material was hot-worked, forged and heat-treated to 160 kp/mm² (230,000 psi) (13-14).⁵ Samples were 46-cm round upset disks austenized at 1,010°C (1850°F) for 25 minutes, oil-quenched, and tempered for 2+2 hours. Each value is the average of 3 tests (25).

OTHER HIGH-CARBON STEELS

Spring Steels

Limited electroslag remelting experience with En 42B, a British 0.70-percent carbon spring steel, has shown that oxygen, sulfur, and silicon were reduced 50, 80, and 42 percent, respectively. Improvements in transverse ductility and reduced anisotropy on a wrought product were also noted. Specifically, impact properties were nearly isotropic in electroslag-remelted material, whereas this was not the case in air-melted En 42B (16).

In another study on a Soviet carbon spring steel, Belov and Tufanov (6) demonstrated that vacuum-induction and electroslag-remelted material possessed greater corrosion resistance in various acids and bases than material melted in open induction furnaces. This was attributed to fewer observed nonmetallic inclusions in vacuum-induction and electroslag-remelted steel.

Bearing Steels

The electroslag process is well suited for remelting bearing steels which require high density, uniform structure, and minimal nonmetallic in-

clusions. Latash and Medovar (23) demonstrated greater densities in six bearing steels after electroslag remelting, compared with air-melted material (averaging 7.84 and 7.74 g cm⁻³, respectively). Fewer oxide and sulfide inclusions (by more than 60 percent) were also noted in Soviet electroslag-remelted steels ShKh15 and ShKh15 SG compared with air-melted material (23). In a British bearing steel (En31=AISI 52100), thin sulfide inclusions⁵ were reduced from 220 to 6 by electroslag remelting. Heavy sulfides decreased from 30 to 2, while aluminates, silicates, and oxides were not significantly present in either electrode or electroslag-remelted material (10). The improved fatigue life of electroslag-remelted bearing steels is believed to result from fewer nonmetallic inclusions. In addition, a twofold to threefold increase in service life of bearing steels was noted compared with conventionally air-melted material (23).

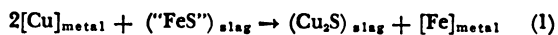
Control of ingot chemistry presents no problems during electroslag remelting of bearing

⁵ Number of inclusions in 25 fields at 400x on a 1 1/8-inch-diameter ball.

steel. Beneficial reductions in oxygen (20 to 10 ppm), sulfur (0.012 to 0.007 percent), silicon (0.35 to 0.27 percent), aluminum (0.009 to 0.005 percent), and nitrogen have been demonstrated as a result of electroslag remelting En31.

SCRAP STEEL

In recent years, the steadily accumulating amount of undesirable copper present in steel as a result of recycling has been a source of concern in effective scrap utilization and the overall solid-waste problem. Acceptable steel industry scrap should contain less than 0.1 weight-percent copper (29). Above approximately 0.2 weight-percent, hot shortness with crack initiation at the edge during rolling operations often results.⁶ No completely satisfactory method has as yet been developed to effectively remove copper from liquid ferrous material. Previous work in steel-making directed toward solving this problem concentrated on removing copper by a suitable solvent or by formation of a copper compound. In the reaction,



at liquid iron temperatures, the sulfur tends to combine with copper rather than iron. This is the basis for most of the aforementioned previous work. Sources of sulfide in the slag have included various alkali and alkaline earth sulfides and sulfates (22, 24, 32).

Since the electroslag process has proven its effectiveness in selectively removing certain undesirable impurities, depending on melting parameters and flux components, the possibility of removing copper from steel scrap by electroslag techniques was suggested. Accordingly, electroslag melting tests were conducted at the Albany Metallurgy Research Center as part of an overall solid waste utilization program of the Bureau of Mines. The objective was to process low-quality steel scrap, particularly junked automobiles, into satisfactory ingot steel. This requires copper removal.

Although the electroslag process was recognized as a relatively expensive approach to processing scrap metal, it was also recognized that for special applications requiring high-purity iron, the process might show promise. Furthermore, no troublesome refractories are required for the process and there was no report of anyone having previously applied the method to refine scrap metal.

⁶ Another approach to this problem is to use coatings to eliminate hot-cracking during working (8).

A small electroslag furnace such as that described in chapter 7 was used in all of the melts. In later heats, the water-cooled copper mold was replaced by a mild steel mold to minimize extraneous copper sources which could contaminate the ingot. Melting procedures followed those outlined in chapter 7. Both dc and ac power sources were used in the melts, all of which were conducted in air.

Flux Selection

A general-purpose composition in the CaF_2 - CaO system provided the basis for all of the fluxes used in this study. Among possible suitable flux additions to remove unalloyed copper in scrap steel, only iron sulfide [equation (1)] shows promise, based on thermochemical calculations (11). All other common copper compounds (for example, sulfides, halides, sulfates, carbonates) are thermodynamically unstable relative to possible flux additions (11-12, 34). However, a few alkali and alkaline earth sulfides and sulfates have considerable mutual solubility with dissolved copper compounds in iron and steel (22, 24, 29, 32), and hence are likely candidates for flux additions to enhance copper removal in the electroslag process. Langenberg and Lindsay (22) demonstrated that copper in experimental iron baths can be reduced by as much as 75 weight-percent with Na_2S additions at high temperatures. The mutual solubility of Cu_2S and Na_2S at high temperatures undoubtedly plays a role. The Cu_2S was formed by initial additions of FeS to the iron. Makar and Dunning (24) have observed that Na_2SO_4 additions to iron resulted in copper reductions of up to approximately 75 weight-percent at 1,300° to 1,650° C. This reduction can also be achieved with thorough flux-metal mixing and with sufficient quantity of slag, on a commercial scale in a cupola (32). Additions of Na_2CO_3 were also made to reduce residual sulfur in the metal, which is increased with the use of sulfur-bearing fluxes, especially in low-carbon melts (29). Mixtures of alkali- and alkaline-earth sulfates (K_2SO_4 , Na_2SO_4 , and CaSO_4) also were shown to remove copper, but not as effectively as undiluted Na_2SO_4 . Safiah and Sale (29) determined that Na_2SO_4 more effectively removes copper in iron melts which contain greater concentrations of carbon. This is explained by an increase in the activity of copper in iron melts with increasing carbon contents as a result of a greater tendency toward liquid immiscibility. A corresponding loss of sodium from the flux due to volatilization and reoxidia-

tion by the atmosphere was also observed (29). This is required to maintain electroneutrality and is detrimental to refractories, which are of no concern in the electroslag process.

Based on the aforementioned consideration, Na_2S , Na_2SO_4 (with Na_2CO_3), FeS , and CaS were among the flux components added in the Bureau of Mines study. Burnt lime was heated to approximately 950°C for several hours to remove moisture and CO_2 . The heated powder was blended with CaF_2 powder, together with any flux additions in the desired amounts. Flux additions were calculated in excess of the stoichiometric amount required to remove all copper in the electrode material. Typically 1,000 to 1,200 grams of dry flux were added to each melt after arc initiation.

Electrode Material

Electrode sources used included (1) reinforcement rods, which had been hot rolled from steel melted from auto scrap and partially reduced iron ore, and which were welded into a cluster approximately 5 cm in diameter, (2) laminated strips of auto body tops which had been either untreated, partially incinerated to remove paint, completely incinerated, or sandblasted, (3) bundled ferrous scrap which had been hot press-forged at 816°C ($1,500^\circ\text{F}$), and (4) gray cast iron to which 1.1 weight-percent copper was added in the form of wire prior to casting.

Melting Parameters

Melts were conducted using 2,000 to 2,500 amperes at 25 to 35 volts for 9.5- to 10-cm-diameter ingots. Melting rates averaged approximately 1.0 kg min^{-1} . For the 25-cm-diameter ingots, 7,000 to 8,000 amperes at 40 volts were used.

Results

Table 39 presents important analytical results of selected electroslag melts, together with comments on the resulting ingots. Several ingot surfaces and longitudinal unetched sections are shown in figures 83, 84, 85, and 86. It is evident that the desired copper removal was not attained under the present experimental conditions regardless of the flux composition or crucible used. Decreases in phosphorus, silicon, and manganese were noted, however. Except when sulfides were added to the flux, reductions in ingot sulfur contents were also obtained. The decrease in manganese can be controlled by the addition of that element in the form of sulfides or halides

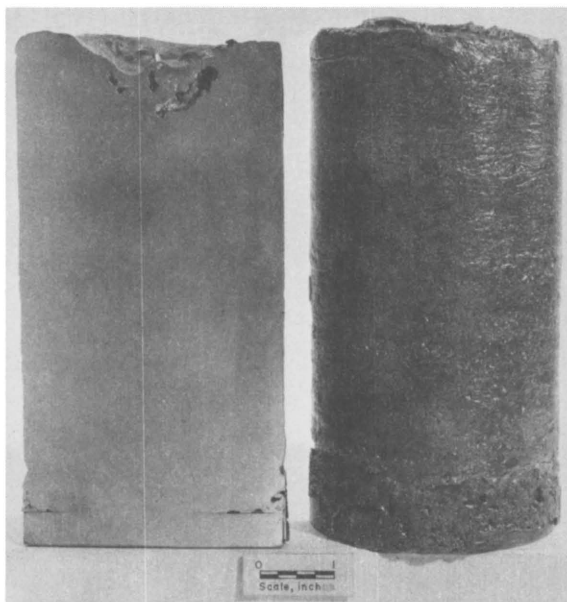


Figure 83.—Ingot halves from electroslag melt 1 (table 39) of reinforcement bar steel using a $70\text{CaF}_2\text{-}30\text{CaO}$ flux.

to the flux, as was noted in several electroslag melts not listed in table 39. All flux additions except CaS tend to result in (1) more erratic melts, (2) porous ingots, (3) rough ingot sur-

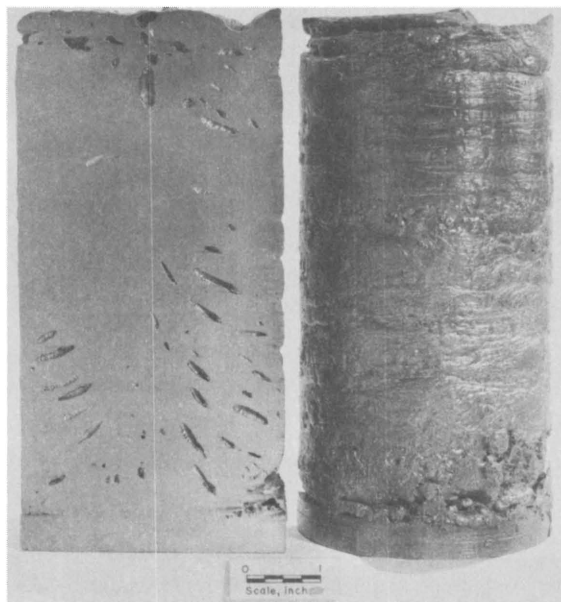


Figure 84.—Ingot halves from electroslag melt 3 (table 39) of reinforcement bar steel with FeS added to the flux.

Table 39.—Results of dc electroslag melting scrap steel with and without flux additions

Impurities, wt-pct										
	C	Cr	Cu	Fe	Ni	Mn	P	S	Si	Remarks
MELT 1: REINFORCEMENT ROD ELECTRODE, 70 CaF ₂ —30 CaO FLUX MILD STEEL CRUCIBLE										
Electrode ¹	0.29	ND	0.61	Major	ND	ND	0.013	0.025	0.090	Sound ingot with good surface and minimal porosity (fig. 83) .
9.5-cm-diam ingot ²	.22	<0.1	.64	Major	<0.1	0.97	.003	.019	.015	
Unused flux	NA	ND	<2x10.4	<0.05	ND	.59	NA	NA	<.79	
Used flux	NA	ND	.013	ND	ND	<.03	NA	NA	ND	
MELT 2: REINFORCEMENT ROD ELECTRODE, 80 CaF ₂ —20 CaO FLUX COPPER CRUCIBLE										
Electrode	0.29	ND	0.61	Major	ND	0.97	0.013	0.025	0.090	Good ingot surface; porous top inside. Av BHN=154. Ingot oxygen increased from 55 ppm (electrode) to 346 ppm; H and N remained constant.
10-cm-diam ingot ³	.22	<0.1	.63	Major	<0.1	.53	.082	.015	.010	
Unused flux	NA	ND	<2x10.4	<0.04	ND	<.02	ND	NA	<.86	
Used flux	NA	<.3	.006	2.46	ND	1.87	.058	NA	1-10	
MELT 3: REINFORCEMENT ROD ELECTRODE, 63.6 CaF ₂ —19.7 CaO FLUX MILD STEEL CRUCIBLE										
Electrode	0.29	ND	0.61	Major	ND	0.97	0.013	0.025	0.090	Porous ingot with folds and rough surface; hot-topped (fig. 84) .
9.5-cm-diam ingot ³	.40	<.1	.65	Major	0.21	.49	.001	.425	.011	
Used top flux	NA	<.1	.011	2.66	ND	2.17	ND	NA	1-10	
MELT 4: REINFORCEMENT ROD ELECTRODE, 63.6 CaF ₂ —19.7 CaO FLUX COPPER CRUCIBLE										
Electrode	0.29	ND	0.61	Major	ND	0.97	0.013	0.025	0.090	Ingot with gross porosity and poor surface. Ingot N increased from 56 ppm (electrode) to 66 ppm.
10-cm-diam ingot ³	.27	<.1	.95	Major	<0.1	.43	.001	.39	<.1	
Used top flux	NA	.1-1.	.27	2.61	<.03	2.96	ND	NA	.3-3.	
MELT 5: REINFORCEMENT ROD ELECTRODE 63.6 CaF ₂ —19.7 CaO FLUX MILD STEEL CRUCIBLE										
Electrode	0.32	ND	0.52	Major	ND	0.68	0.080	0.028	0.430	Smooth melt; good ingot surface (fig. 85) .
10-cm-diam ingot ³	.29	<0.1	.44	Major	0.1-1.	.3-3.	.070	.330	.084	
Used flux	NA	<.03	.009	0.91	ND	.62	NA	2.80	.3-30	
MELT 6: REINFORCEMENT ROD ELECTRODE 46.5CaF ₂ —14.5CaO—19.5Na ₂ SO ₄ —19.5 Na ₂ CO ₃ FLUX COPPER CRUCIBLE										
Electrode	0.29	ND	0.61	Major	ND	0.97	0.013	0.025	0.090	Unstable erratic melt; ingot had deep folds and macro-inclusions.
10-cm-diam ingot ³	ND	<0.1	.67	Major	<.1	.10	ND	ND	.1	
Used top flux	NA	.1-1.	.31	14.4	<.1	2.28	NA	NA	.3-3.	
MELT 7: LAMINATED STRIPS, AUTO BODY TOPS (Sandblasted) 76.3CaF ₂ —23.7CaO FLUX MILD STEEL CRUCIBLE										
Electrode	0.06	ND	0.05	Major	ND	0.29	0.006	0.024	ND	Pinhole porosity on outside ingot surface; porous inside (fig. 86) .
10-cm-diam ingot	.22	<0.1	.06	Major	<0.1	.14	<.001	.013	0.01	
Unused flux	NA	ND	<2x10.3	<0.05	ND	<.02	NA	NA	.71	
Used flux	NA	<.1	.01	6.2	ND	1.34	.017	.08	.3-3.	
MELT 8: BUNDLED FERROUS SCRAP 70 CaF ₂ —30CaO FLUX COPPER CRUCIBLE										
Electrode ⁴	0.082	<0.03	0.07	Major	<0.3	0.30	<0.006	0.026	<0.1	Porous ingot with a deep pool and folds on surface. Electrode Zn (1-10 pct) de-
25-cm-diam ingot ³	.013	ND	.14	Major	<.3	<.1	<.001	.010	ND	

Table 39.—Results of dc electroslag melting scrap steel with and without flux additions—Continued

Impurities, wt-pct										
	C	Cr	Cu	Fe	Ni	Mn	P	S	Si	Remarks
MELT 8: BUNDLED FERROUS SCRAP 70 CaF ₂ —30CaO FLUX COPPER CRUCIBLE—Continued										
										creased to <0.1 pct in ingot.
MELT 9: GRAY CAST IRON 64.9CaF ₂ —20.2CaO—14.9Na ₂ S FLUX MILD STEEL CRUCIBLE										
Electrode	3.36	ND	^a 1.10	Major	ND	0.47	0.27	0.07	1.98	Erratic melt; poor ingot surface. Av BHN=357.
10-cm-diam ingot ²	3.1	0.19	1.15	Major	<0.1	.43	.195	.17	1.54	
Used flux	NA	<.1	.12	1.73	ND	.64	.006	2.95	.3–3.	

NA Not applicable. ND Not detected.

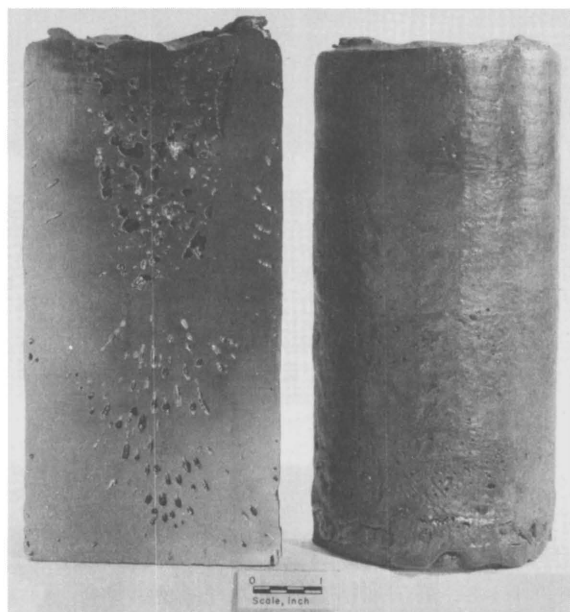
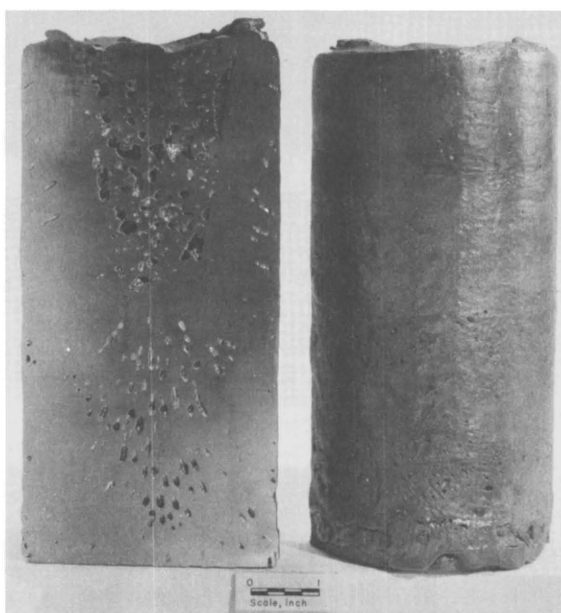
¹ Average of Albany Metallurgy Research Center and Oregon Steel Mills analyses.² Average of 4 locations.³ Average of 3 locations.⁴ Average of 2 locations.⁵ Includes 1 wt-pct Cu added before melt.

Figure 85.—Ingot halves from electroslag melt 5 (table 39) of reinforcement bar steel with CaS added to the flux.

faces, and (4) iron pickup in the flux; see figures 83–85 and table 39. These observations are believed to be related to the high-temperature stabilities of the sulfides. For example, the free energies of formation (kcal mole⁻¹) of CaS, Na₂S, and FeS at 2,000° K are –76, –20 (estimated), and –14, respectively (9, 11). Calcium sulfide also possesses a relatively low vapor pressure in comparison to the others. Decomposition of Na₂SO₄ and Na₂CO₃ at the high temperatures involved probably also contributed to the ingot

porosity and melt instability noted when these compounds were added to the flux. Safiah and Sale (29) indicated that the oxide decomposition of Na₂SO₄ can be suppressed in the presence of excess carbon. The carbon reacts with the sulfate to form Na₂S and CO. This reduction can also be effected by iron when less carbon is present. Other electroslag melts, not reported in table 39, in which 2 to 5 weight-percent foundry carbide (CaC₂+CaO) was added to the flux, have

Figure 86.—Ingot halves from electroslag melt 7 (table 39) of laminated strips of auto body steel using a 76.3CaF₂—23.7CaO flux.

shown that carbon can be retained (but not increased) in the resulting ingots.

In the case of laminated strips of auto body tops, the condition of the electrode (sandblasted, incinerated, or partially incinerated) exerts essentially no influence on the resulting ingot impurities or copper removal. Impurity changes between pretreated electrode and ingot material are similar to those shown in table 39 (melt 7) for untreated auto body material.

Summary

Although copper could not be removed under the electroslag melting conditions used in this initial study, it was shown that scrap steel could be consolidated into ingots, perhaps for remelting or forging where the observed porosity would presumably heal. Some impurity reductions were also noted. Effective copper removal evidently requires a longer reaction time with appropriate sulfur-bearing constituents than that available in the electroslag process. More viscous fluxes may be helpful, although a careful evaluation of derived nonmetallic inclusions in the ingots would be required in this case. Alternatively, use of more stable sulfur-bearing additions such as alkaline-earth sulfates, together with a more rigorous flux pretreatment (for example, fusion) may ameliorate the situation by retaining the sulfur-bearing components in the flux for a longer period of time during melting.

CONCLUSIONS

In this chapter, we have seen that the electroslag remelting process improves ingot quality over that achieved with conventional melting techniques for specialty steels, thus justifying the added expense. Among the benefits cited for electroslag remelting are (1) sulfur removal, with lesser oxygen and silicon decreases, (2) generally fewer and smaller inclusions, (3) directly workable ingot surfaces, (4) improved yield, (5) improved structural and chemical homogeneity, and (6) decreasing anisotropy of mechanical properties. Less dramatic advantages of the electroslag process are observed over other secondary melting techniques such as vacuum-arc remelting and vacuum-induction melting. These include (1) smoother ingot surfaces, (2) greater yield for hot work steels, (3) control of chemical refining, and (4) generally fewer and smaller nonmetallic inclusions, except for large ingots of high-speed steels.

The greatest area for improvement in electroslag process technology for iron and steel lies in the development of large-tonnage ingots with equal properties to those found in smaller ingots. This appears to be the present developmental thrust among electroslag ingot producers throughout the world.

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CHAPTER 13.—ELECTROSLAG REMELTING OF STAINLESS STEEL¹

By W. E. Anable,² R. H. Nafziger, and D. C. Robinson³

As part of the program for developing liquid-metal fast-breeder reactors, the U.S. Atomic Energy Commission requires thin-wall type 316 stainless steel tubing for ultimate use as fuel cladding. One of the objectives of this program is to improve tubing quality through variations in melting practice. As the electroslag process has established itself in the past few years as an important melting practice for specialty steels, the Bureau of Mines was requested to evaluate this process for type 316 stainless steel.

Of particular interest was the opportunity to test the theory that inclusions that are not removed in the electroslag process are reduced in size and dispersed throughout the metal. If this proved true, the expected distinct improvement in metal integrity could reduce irradiation-induced swelling in stainless steel. Swelling caused by fast neutron damage at elevated temperatures is associated with the production of cavities (11). It is generally agreed that these cavities are the result of a combination of two discrete phenomena: (1) Gas-producing neutronic reactions with alloy constituents, and (2) vacancy-producing displacement collisions.

In addition, to meet the requirements for reactor use, ingot segregation, internal defects, and nonmetallic inclusions such as type D globular oxides due primarily to Al_2O_3 should be minimal. In the consumable-electrode vacuum-arc remelting process, the problem of alloy segregation in iron-base alloy ingots increases as the diameter of the ingot and the molten pool become larger. Lowering the melting rate in vacuum-arc remelting to reduce the pool depth leads to a poor ingot surface. On the other hand, the electroslag remelting process for stainless steels can produce smooth ingot surfaces (4), reduce the aforementioned nonmetallic inclusions (1, 4), lead to minimal segregation and internal

defects (4), and reduce silicates in the metal (1). Preferred grain orientation can be obtained by limiting the pool depth through control of the current-voltage relationship, and, therefore, of the heat distribution in the system.

Holzgruber, Peterson, and Schneider (8) have demonstrated that the economics and quality of ac-electroslag-remelted products are superior to those of products melted with dc straight or reverse polarity. In addition to claims for improved sidewalls, preferred grain orientation, and lower impurity content, ac melting appears to improve desulfurization and deoxidation of steels. Sulfide inclusions are largely eliminated, and oxide inclusions are decreased. These advantages of electroslag melting were expected to be realized in the present work.

In the work reported in this chapter, three series of small-scale electroslag-remelted ingots [7.6-cm (3-inch) diameter] were prepared to determine optimum flux composition and melting parameters. Subsequently, thirteen, 12.7-cm (5-inch) diameter by 40.6- to 45.7-cm (16- to 18-inch) long ingots were prepared according to the outline shown in table 40.

This work was carried out in cooperation with the Atomic Energy Commission under Contract AT(11-1)-599, Activity 4420. R. R. Studer of WADCO Corp, provide the technical liaison.

EXPERIMENTAL PROCEDURES

Melting Parameters

Melting parameters and equipment for this work were similar to those discussed in chapter 7. Energy consumption for the small-scale ingots ranged from 1.3 kwhr kg^{-1} for flux 8 to 1.9 kwhr kg^{-1} for flux 1⁴. Large-scale ingot energy consumption ranged from 1.2 kwhr kg^{-1} for flux 1 to 1.9 kwhr kg^{-1} for the CaF_2 flux. Melt rates using the CaF_2 flux were approximately half those of the oxyfluoride fluxes shown in Table 41. VAR ingots required an average energy con-

¹ Adapted from J. Metals, v. 25, November 1973, pp. 55-61.

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⁴ For the compositions of these fluxes, see table 41.

Table 40.—Program for electroslag remelting of type 316 stainless steel large-scale ingots

WADCO ingot No.	Ingot description
4 INGOTS FROM AIR-MELTED 316 STAINLESS STEEL (ELECTRODE SAMPLE 1)	
1	As-received, air-melted ingot as a blank.
2	Electroslag-remelted ingot using the preferred slag (50CaF ₂ -30CaO-20Al ₂ O ₃).
3	Vacuum-arc-remelted ingot, as-received.
4	Vacuum-arc-melted ingot after electroslag remelting with preferred slag.
4 INGOTS FROM DOUBLE-VACUUM-MELTED 316 STAINLESS STEEL (ELECTRODE SAMPLE 2)	
8	Electroslag-remelted ingot using CaF ₂ .
9	Electroslag-remelted ingot using the preferred slag.
10	Electroslag-remelted ingot using 70CaF ₂ -30CaO slag.
11	Vacuum-arc-remelted ingot after electroslag remelting with preferred slag.
5 INGOTS FROM ELECTRON-BEAM REMELTED 316 STAINLESS STEEL (ELECTRODE SAMPLE 3)	
5	Electroslag-remelted ingot with CaF ₂ .
6	Electroslag-remelted ingot with preferred slag.
7	Vacuum-arc-remelted ingot after electroslag remelting with preferred slag.
12	Electroslag-remelted ingot using the preferred slag and aluminum additions to slag.
13	Same as 12, but followed by vacuum-arc-remelting.

Table 41.—Flux compositions used in electroslag melting of small-scale type 316 stainless steel ingots, wt-pct

Flux	CaF ₂	CaO	MgO	Al ₂ O ₃
1	50	30	0	20
2	60	20	0	20
3	70	10	0	20
4	80	20	0	0
5	0	45	0	55
6	50	20	0	30
7	18	25	17	40
8	70	0	0	30

sumption of 0.7 kwhr kg⁻¹. Ingot preparation for macro and micro structure studies and chemical analysis followed well-established procedures.

Electrode Material

Type 316 stainless steel electrode material was received from three sources. Sample 1 was prepared in a conventional three-phase electric steel-making furnace by a commercial producer. A standard production heat using a computer-controlled operation and the best available commercial scrap and alloying additions was used. Sample 2 was commercially prepared from electrolytic manganese, electrolytic chromium, ferromolybdenum, ferrosilicon, and low carbon-low sulfur iron. The charge was first melted in a vacuum-induction furnace lined with 96-percent MgO refractory. The furnace pressure was main-

tained at less than 1.5×10^{-1} torr. The 35.6-cm-diameter ingot was vacuum-arc-remelted into a 40.6-cm-crucible at pressures of less than 1.6×10^{-2} torr. This ingot was reheated to 1,204° C (2,200° F), forged to 14.6-cm diameter, and machined to produce a 11.4-cm-diameter billet. The detailed processing history of the third source material is unknown. Presumably, this sample was vacuum-melted 316 stainless steel (comparable to sample 2 material) which had been further remelted in an electron-beam furnace. Chemical analyses of the three samples are given in table 42.

Table 42.—Analyses of type 316 stainless steel electrode stock, wt-pct

Element	Sample 1 ¹	Sample 2 ²	Sample 3 ³
Cr	16.8	16.5	16.0
Ni	13.3	13.2	14.7
Mn	1.54	1.40	.05
Mo	2.30	2.99	2.66
Si	.61	.40	.44
C	.021	.04	.028
S	.011	.014	.006
P	.015	.017	.01
O	.0104	.0030	.0008
N	.0266	.0170	.0060
H	.0004	.0003	.0001

¹ Air-melted material.

² Double-vacuum-melted material.

³ Electron-beam-remelted material.

Flux Selection and Preparation

The eight flux compositions for melting the small-scale ingots (table 41) were selected on the basis of estimated liquidus temperature, variations in physicochemical properties, known refining capabilities, and other properties summarized in chapter 6. Fluxes were prepared from commercially available CaF_2 , CaO , MgO , and reagent-grade Al_2O_3 . These components were preheated, blended in the desired proportions, reheated, and fused in a graphite resistor furnace prior to use.

The large-scale melts were restricted to the evaluation of three fluxes: (1) CaF_2 , (2) $50\text{CaF}_2-30\text{CaO}-20\text{Al}_2\text{O}_3$, and (3) $70\text{CaF}_2-30\text{CaO}$. In each instance the weight of flux was adjusted to provide about 5.1 cm of molten flux on top of the ingot at the conclusion of the run. Adjustments were based on the densities of the molten fluxes; see chapter 6.

Ac Versus dc Power

The inconclusive results of electroslag remelting using straight-polarity dc prompted additional melts with single-phase ac power. For the ac melts, only sample 1 electrode stock (air-melted) was used with the eight slags because changes in the alloy structure and composition due to electroslag remelting were recognized most easily with this material. All large-scale ingots were melted with ac power to minimize oxygen contamination and reduce nonmetallic inclusions in the metal.

RESULTS OF SMALL-SCALE MELTS

Ingot Impurities and Alloy Constituents

Table 43 summarizes the results of impurity contents in the small-scale electroslag-remelted ingots. Flux numbers correspond to the compositions given in table 41 and furthermore represent ratings based on a weighed evaluation of electroslag-remelted ingot inclusions, impurity levels, macrostructure, and ingot surface. Flux number 1 is the preferred composition, with the other fluxes ranked in descending order.

The range of recoveries of the alloying constituents were, in weight-percent, C, 83 to 90; Cr, 96 to 98; Mn, 96 to 98; Mo, 99 to 100; Ni, 98 to 99; and Si, 77 to 84.

Microstructure

Mixed globular oxides (spherical particles) and alumina clusters (groups of irregularly shaped particles) were present in the as-received material from both electrode samples 1 and 2.

Electroslag melting sample 1 with ac power showed the greatest improvement in microstructure. Representative specimens are shown in figure 87. Dispersion of both types of inclusions after electroslag remelting is evident. Alumina inclusions were minimized by remelting the fluxes containing 20 weight-percent alumina or less. The use of fluxes with 30 to 55 weight-percent alumina resulted in more alumina clusters and globular oxides in the ingots. Both alumina clusters and globular oxides were present in samples remelted with the $45\text{CaO}-55\text{Al}_2\text{O}_3$ flux.

Inclusion counts [ASTM-E-45(D)] for small-scale electroslag-remelted ingots are summarized in table 44. The alumina clusters are often larger than globular oxides and frequently appear at the edge of ferrite grain boundaries.

Electron Microscope and Microprobe Results

One specimen from each electroslag-remelted ingot was polished using picric-hydrochloric acid in ethanol and then electrolytically etched with perchloric acid in ethanol before examination by the two-stage plastic-carbon replica technique at X 1,900.

All samples contained a ferrite phase, which contained more molybdenum and chromium and less nickel than the matrix. A typical analysis of this phase is, in percent, Cr, 23; Mn, 1.5; Mo, 6; and Ni, 8.5. Traces of alumina, calcium fluoride, and chromium carbide were found associated with the ferrite at the grain boundaries. The ferrite present in the austenite structure appears cleaner in ac-melted samples than in the dc series. Microprobe studies reveal that MnS was occluded in the ferrite grain boundaries of dc-melted samples, but none was observed in the ac-melted samples. The lower oxygen and sulfur levels that characterized the ac series and the cleaner microstructure account for the lower grain-boundary contamination. More porosity was present in ingots remelted with binary fluxes than with ternary fluxes.

Ingot Macrostructure

A representative ingot macrostructure is shown in figure 22. Limiting the power to 30 to 35kw resulted in a shallow pool that permitted the columnar grains to form more or less vertically. Ingot surface improved when ac power was used. The use of CaF_2 -base fluxes containing 10 to 30 percent CaO and 20 to 30 percent alumina produced ingots with better surfaces than those obtained in ingots melted with fluxes without

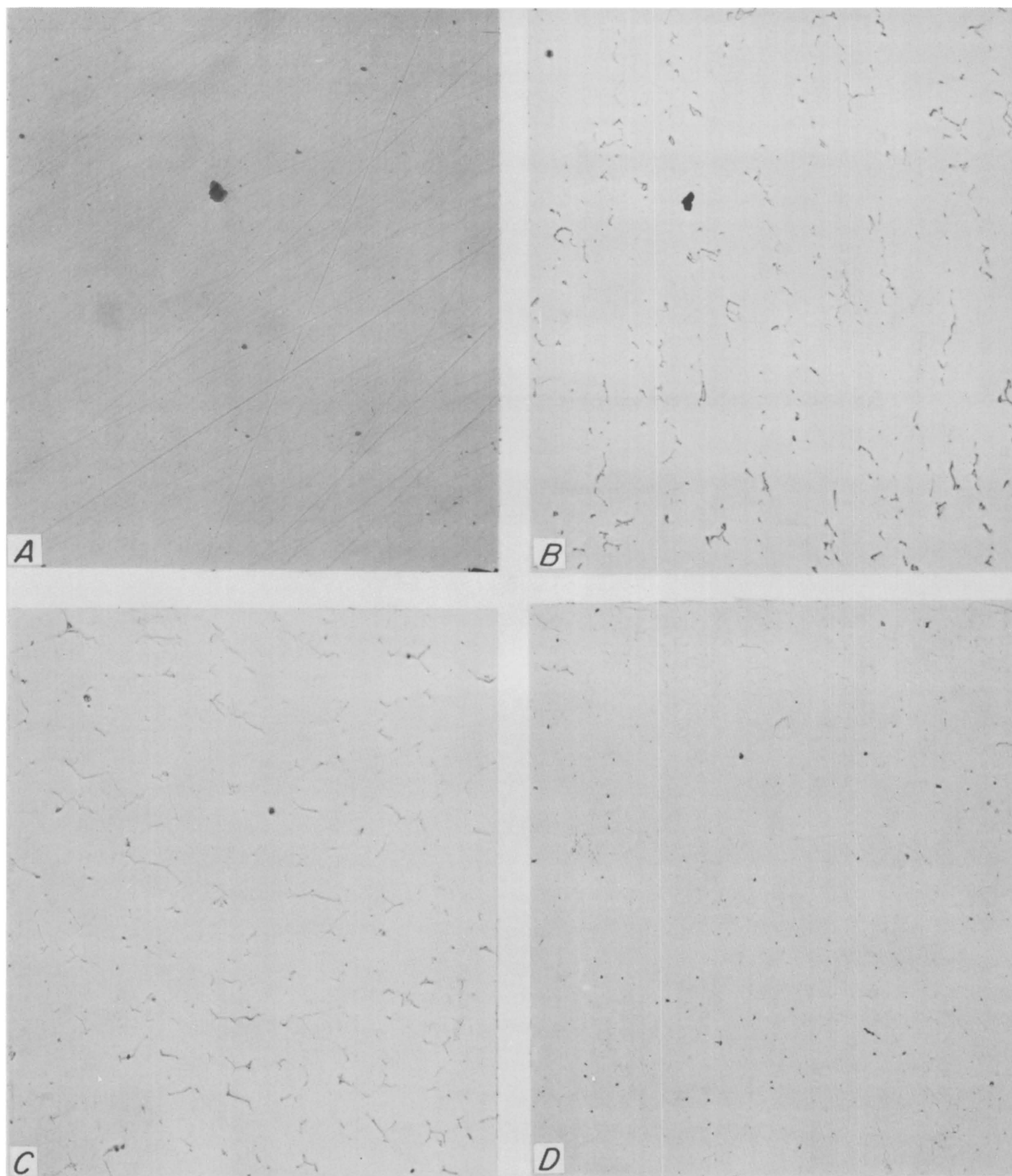


Figure 87.—Microstructure before and after ac electroslag remelting type 316 stainless steel from electrode sample 1 (air-melted, as-polished, X 100).

A, As-received material; no visible ferrite.

B, After remelting with 50CaF₂-30CaO-20Al₂O₃ flux; the ferrite phase shows as irregularly shaped particles.

C, After remelting with 60CaF₂-20CaO-20Al₂O₃; note inclusion dispersion and reduction in size.

D, After remelting with 70CaF₂-10CaO-20Al₂O₃ flux.

alumina or those containing 40 to 55 percent alumina. This phenomenon is probably related to the formation of $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$, which is present at liquidus temperatures when the alumina content is greater than 10 weight-percent in the $\text{CaF}_2\text{-Al}_2\text{O}_3$ system (14). The liquidus temperatures for compositions with greater than 20 weight-percent Al_2O_3 are above the melting range of type 316 stainless steel ($\sim 1,371^\circ$ to $1,399^\circ$ C). Such a high-melting primary phase is believed to be conducive to good ingot surface (5). The liquidus temperatures of fluxes with 40 weight-percent Al_2O_3 or more are probably too high to promote satisfactory ingot surfaces.

The hardness of the ingots prepared by electroslag remelting ranged from RHN B-63 to B-77.

RESULTS OF LARGE-SCALE MELTS

Ingot Impurities

Gas analyses and ingot aluminum contents for the large-scale electroslag-remelted 316 stainless steel ingots are given in table 45. The composition of "as-received materials" was adjusted by adding chromium, manganese, and carbon to the electrode material to meet the nominal composition for 316 stainless steel and to account for melting losses. Alloying constituent ranges

Table 43.—Summary of impurity contents (ppm) for small-scale electroslag-remelted type 316 stainless steel ingots

	Electrode sample 1 ¹					Electrode sample 1 ²					Electrode sample 2 ²				
	Al	H	N	O	S	Al	H	N	O	S	Al	H	N	O	S
Electrode stock	<500	4	266	104	110	<500	4	266	104	110	<500	3	170	30	140
Flux number:															
1	750	9	260	30	<20	1,000	7	235	103	30	750	8	148	109	80
2	650	7	280	30	<30	550	7	264	58	50	700	2	164	91	70
3	550	3	260	58	80	1,150	4	263	103	50	1,100	2	167	131	70
4	<500	4	268	18	40	<500	3	277	64	70	<500	3	200	100	35
5	650	6	267	72	45	550	5	273	128	60	800	4	148	126	70
6	850	6	265	60	55	950	5	320	120	40	800	1	161	103	80
7	<500	4	274	60	75	750	2	287	79	90	600	6	148	106	<50
8	<500	3	277	55	85	1,700	3	280	98	100	1,050	3	185	74	35

¹ Electroslag-remelted with ac power.

² Electroslag-remelted with dc power.

NOTE.—Melts using dc power were conducted with 1,500 to 1,700 amperes at 20 to 24 volts under 1/3 atm backfilled helium and 0.6 kg fused flux. Power parameters for ac melts were 1,200 to 1,500 amperes at 26 to 28 volts.

Table 44.—Inclusion ratings at X100 for small-scale ingots according to ASTM-E-45(D)¹

	Electrode sample 1 ¹				Electrode sample 1 ²				Electrode sample 2 ²			
	Alumina clusters		Globular oxides		Alumina clusters		Globular oxides		Alumina clusters		Globular oxides	
	Thin	Thick	Thin	Thick	Thin	Thick	Thin	Thick	Thin	Thick	Thin	Thick
Electrode sample	0	0	2½	½	0	0	2½	½	0	0	½	0
Flux number:												
1	0	0	1	0	½	0	1	½	½	0	1	0
2	0	0	1	0	½	0	1	½	0	0	1	0
3	0	0	1	0	0	0	1	0	1	0	1	½
4	0	0	1	0	0	0	½	0	0	0	1	½
5	½	0	1½	½	½	0	1½	½	½	0	1½	0
6	0	0	1	0	½	½	1	0	½	½	1	0
7	0	0	1½	0	0	0	1	0	0	0	1	0
8	0	0	1½	0	½	0	1	0	0	1	1½	0

¹ Normally, sulfides and silicates would be included in this tabulation. However, these inclusions were not identified in the samples and therefore were not entered.

² Electroslag-remelted with ac power.

³ Electroslag-remelted with dc power.



Figure 88.—Macrostructure of a small-scale ingot remelted with 70CaF_2 - 10CaO - $20\text{Al}_2\text{O}_3$ flux and ac power. The surface was polished and etched with FeCl_3 in HCl .

for these ingots were, in percent, C, 0.044 to 0.058; Cr, 17.1 to 17.8; Mn, 1.51 to 2.00; Mo, 2.26 to 3.00; Ni, 13.1 to 13.7; P, 0.007 to 0.021; S, 0.003 to 0.007; and Si, 0.31 to 0.53.

Microstructure

The ingot size has a minimal effect on the size reduction and dispersion of nonmetallic inclusions after electroslag remelting. Globular oxides in electrode sample 1 were reduced in size by a factor of two after electroslag remelting with slag 1. When viewed at X 1,900 magnification, alumina and sulfide inclusions were not observed, and the grain boundaries appeared to be clean, as shown in figure 89. The same observa-

Table 45.—Aluminum and gas analysis of large-scale ingots, ppm

WADCO ingot No.	O	N	H	Aluminum ¹	
				Top	Bottom
1	104	266	4	<500	<500
2	30	262	7	<500	700
3	89	273	2	<500	<500
4	29	250	3	<500	600
8	41	160	5	<500	<500
9	50	204	8	<500	900
10	28	165	2	<500	<500
11	31	161	3	500	800
5	47	591	2	<500	<500
6	23	620	5	<500	700
7	38	477	2	<500	<500
12	27	554	4	<500	² 1,600
13	32	449	2	<500	² 1,000

¹ Analyses of electrode material are given in table 43.

² Aluminum added to flux in an attempt to reduce globular oxides.

NOTE.—Melts were conducted with ac power using 2,400 amperes at 28 volts. Vacuum-arc-remelted ingots (table 40) were prepared with 3,400 to 4,000 amperes dc at 25 to 27 volts.

tions apply to electroslag-remelted ingots from electrode samples 2 and 3 (table 42), using flux 1 (fig. 89). In electrode sample 2, remelted with the 70CaF_2 - 30CaO flux, the ferrite grains increased in size by a factor of two over those in the electrode stock. Only globular oxides, which ranged from 1 to 3 micrometers in diameter, were observed. Large-scale ingots electroslag-remelted from electrode samples 2 and 3 with the CaF_2 flux appeared relatively free of inclusions at X 100. At X 1,900, however, more inclusions (3 to 7 micrometers in diameter) were observed in ingots melted from electrode sample 3 than in those from sample 2. The structure of the latter ingot was characterized by large ferrite grains in austenite. This can be attributed to the slower melting rate noted previously when the CaF_2 flux was used.

Ingot Sidewall

Large-scale ingot sidewall quality was satisfactory and comparable to that of small-scale ingot sidewalls. However, when the 70CaF_2 - 30CaO flux was used, a thick flux layer formed between the crucible and the ingot, resulting in a rough sidewall and no top flux. Increasing the power and amount of flux resulted in a satisfactory melt (sufficient top slag was present) at 21 volts and 3,400 amperes. The ingot surface would still require machining prior to fabrication, however.

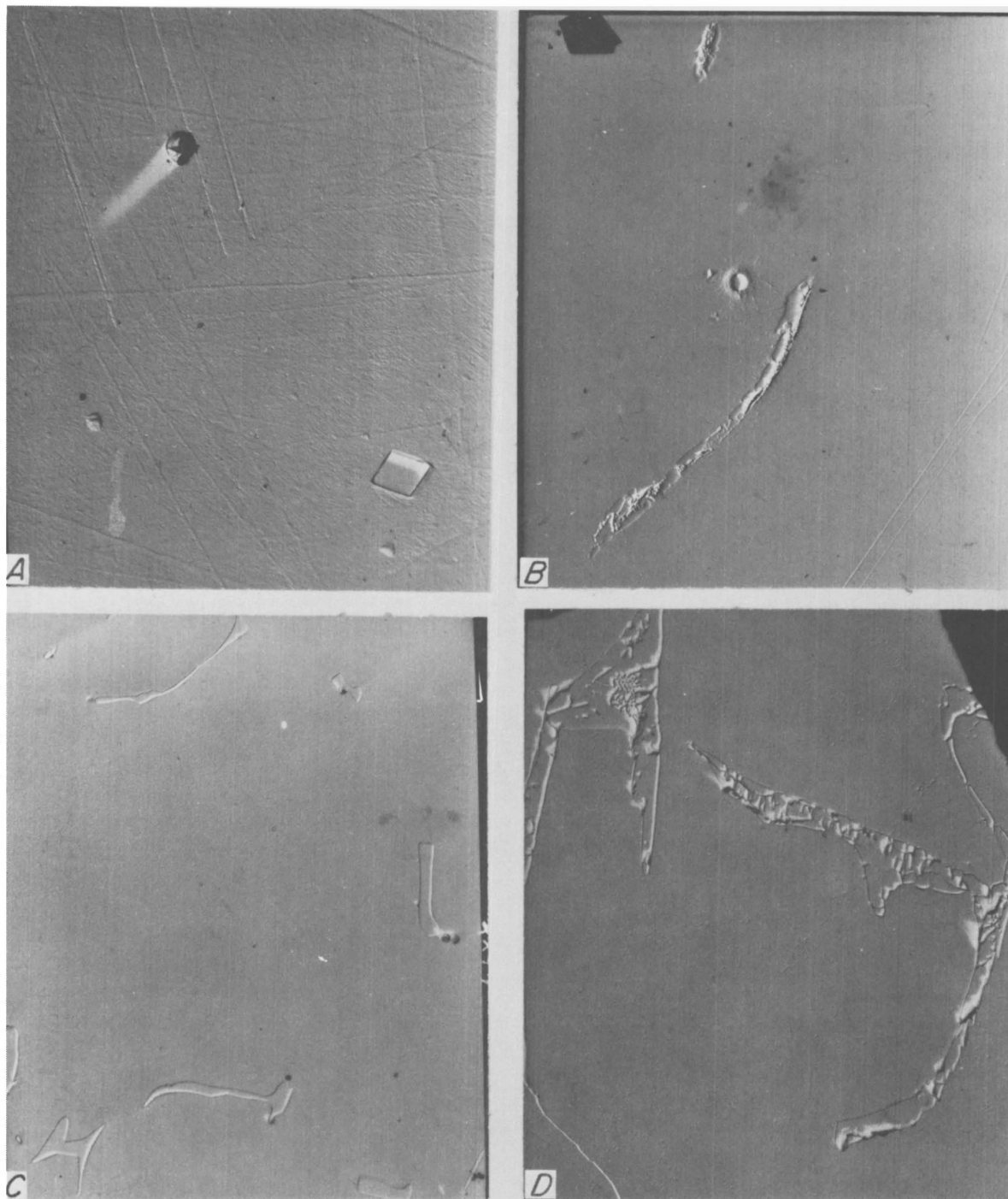


Figure 89.—Microstructure of stainless steel before and after electroslag remelting large-scale ingots with flux 1 (X 1,900).

- A, Electrode sample 1 before electroslag remelting; the euهدral grain in the upper left is an inclusion, whereas the other large defect is a hole.**
- B, Electrode sample 1 after remelting; two defects are obvious to the left of the ferrite phase.**
- C, Electrode sample 2 before electroslag remelting.**
- D, Electrode sample 2 after remelting.**

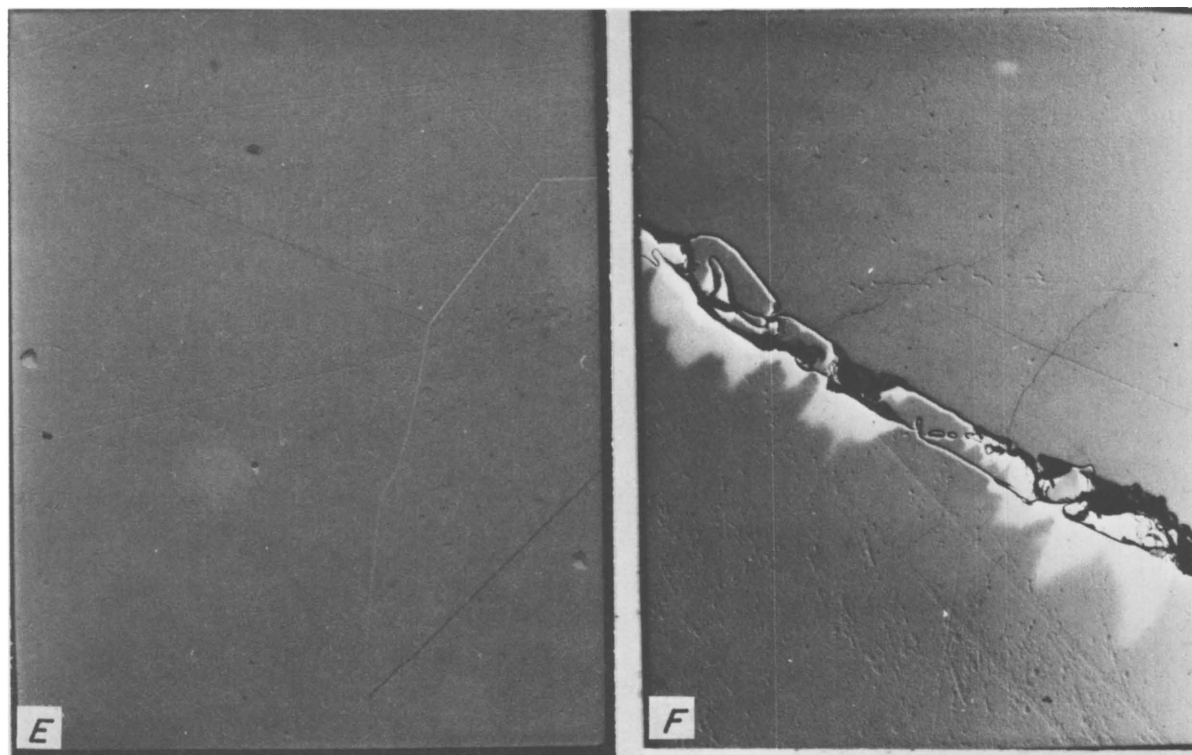


Figure 89.—Microstructure of stainless steel before and after electroslag remelting large-scale ingots with flux 1 (X 1,900) (Con.).

E, Electrode sample 3 before electroslag remelting; note the absence of defects in this material.
F, Electrode sample 3 after remelting.

ELECTROSLAG REMELTING OF STAINLESS STEELS IN OTHER COUNTRIES

In the Soviet Union, the Dnieprospetzstal plant in Zaporozhje is currently producing stainless steel slab ingots up to 4 tons by the electroslag process. Several papers have appeared in the literature by Soviet authors citing improvements and greater isotropy of mechanical properties (including tensile and impact strengths and ductility) of electroslag-remelted stainless steel in contrast to electric-arc-melted material (9–10, 12–13). Smoother sidewalls (12), threefold decreases in nonmetallic inclusions (9, 12–13), and lower sulfur, silicon, oxygen, and nitrogen contents (9–10) have been observed in electroslag-remelted stainless steel ingots in contrast to those melted by conventional processes. The Soviets have also added 5 to 10 weight-percent Na_2O to 70CaF–30 Al_2O_3 fluxes during electroslag remelting of stainless steels. This addition decreases the viscosity of the flux, promotes intense

bath stirring, encourages formation of a thin flux skin, and stabilizes the flux bath temperature. The result is a smooth ingot surface which reduced losses by 10 percent. Mechanical properties were also said to be improved (16).

West German authors have reported on electroslag-remelted stainless steels and claim reduction in segregation, greater yield, improved ductility, fewer inclusions, and reduction in anisotropy of mechanical properties in comparison with material melted either in a consumable-electrode arc furnace or by the electron-beam process (19–20). It has been noted that electroslag remelting of a 20 percent Cr–10 percent Ni–1.5 percent Cb stainless steel raised the maximum temperature for hot deformation of wrought products from 1,050° to 1,100° C compared with electric-furnace-melted material (6). In Avesta, Sweden, high-quality stainless steel ingots are produced by the electroslag process (17). Beneficial effects on the corrosion resistance of electroslag-remelted stainless steels as compared with

steels melted in electric arc and induction furnaces have been observed (3,18).

Research at the Japanese Iron and Steel Institute, using CaF_2 -based fluxes, has shown improvement in ductility, inclusion reduction, and desulfurization for electroslag-remelted stainless steels (15). Mitchell and coworkers (2) in Canada have successfully electroslag-remelted 321 stainless steel under CaF_2 -20 weight-percent YF_3 fluxes on a laboratory scale in an argon atmosphere. A finite cylindrical liquid depth conducive to smooth ingot surfaces was observed. In this country, researchers have designed a statistical study which showed little evidence of macrosegregation with a constant composition along ingot lengths when three grades of stainless steel were electroslag-remelted. Fluxes contained from 17.5 to 40.0 weight-percent CaF_2 (7).

CONCLUSIONS

Electroslag remelting of type 316 stainless steel disperses the nonmetallic inclusions and reduces the microporosity in 7.6 and 12.7-cm-diameter ingots. Both the larger globular oxides and the alumina clusters were reduced in size by a factor of two, and they were difficult to discern at X 100 after remelting. Alumina inclusions were minimized in ingots remelted with fluxes having no more than 20 percent alumina. An occasional sulfide inclusion was observed in ingots remelted with dc power. However, neither sulfide nor silicate inclusions were observed in samples at X 100 or X 1,900 after remelting with ac power.

Power from an ac source was shown to be more effective than dc power in (1) producing a cleaner microstructure, (2) lowering the ingot

aluminum, sulfur, and oxygen content, and (3) producing an ingot with directly forgeable surfaces. The nitrogen, phosphorus, and hydrogen contents remained nearly constant under the molten flux cover, whereas the presence of 10 to 30 percent lime effected desulfurization of the molten alloy, as expected. More than 20 percent alumina in the flux resulted in higher residual aluminum content (>0.05 percent), and the oxygen increased from 30 ppm to 50 to 100 ppm. There was little loss of alloying addition during electroslag remelting. Recoveries were in percent, >95 for Cr, Ni, Mn, and Mo; Si, ~ 83 ; C, 90 to 92; S, 34 to 66; and P, ~ 89 . Microprobe studies showed that the manganese sulfide, which was occluded in ferrite grain boundaries after remelting with dc power, was not observed at X 1,900 after electroslag remelting with ac power.

Comparative melts conducted with CaF_2 and 70CaF_2 -30CaO demonstrated that both fluxes were inferior to ternary slags in the CaF_2 -CaO- Al_2O_3 system. Ingots remelted with CaF_2 had satisfactory surfaces, but more globular oxide inclusions were present than desired. In addition, the melting rate for the same power input was about half of that for flux 1 (50CaF_2 -30CaO-20 Al_2O_3). The 70CaF_2 -30CaO flux produced the desired ingot microstructure, but with exceedingly rough and uneven surfaces.

The shallow pool resulting from limiting the power to 30 to 35 kw in the small-scale melts resulted in nearly vertical columnar grains. A compromise was thus established between the desired microstructure and the general surface appearance. Higher power inputs generally produced a smoother ingot surface.

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CHAPTER 14.—ELECTROSLAG REMELTING OF SUPERALLOYS¹

By R. H. Nafziger and R. L. Lincoln²

For certain uses of materials, such as in jet engines and gas turbines, the ability to withstand high temperatures without melting or corroding and to support stress at such temperatures is of prime importance. Superalloys in which nickel-chrome alloys have been strengthened by the precipitation of Ni₃(Ti, Al)-type intermetallic compounds were first used for such applications with considerable success. Solution-strengthened nickel-base alloys which normally contain manganese and nitrogen were later developed. In addition, other iron- and cobalt-base superalloys have been used successfully in high-temperature atmospheres.

Although the most common secondary melting techniques for these alloys have been vacuum-arc or vacuum-induction processes, electroslag remelting is becoming more common. Improved yield, workable ingot surfaces, solidification control to minimize segregation, improved hot workability, improvement in some mechanical properties, and close control of ingot chemistry have been cited as advantages of the electroslag process for remelting superalloys.

As the molten pool depth can be closely controlled during electroslag remelting, the growth direction of columnar grains can be established. During the electroslag remelting of superalloy ingots, shallow molten pools are typical. This gives rise to columnar grain alignments more parallel to the longitudinal axis of the ingots since grain growth is perpendicular to the solid-liquid interface (25). Superior hot workability has been demonstrated in electroslag-remelted superalloy ingots as compared with vacuum-arc-remelted material. Hot ductility also was superior, giving rise to better forgeability (11, 25). Such improvements in these properties are believed to be due to the macrostructure obtained in ingots remelted by the electroslag

melting process. Improved hot ductility results in higher yield and therefore in better productivity, and a more economical operation.

As noted previously in this Bulletin, the electroslag process provides a means to closely control ingot solidification rates; this in turn influences the degree of segregation, an important consideration when melting superalloys. Axial grain orientation which is more easily attainable in electroslag melting, combine with high rates of solidification to minimize the formation of segregation defects such as freckles (10). In addition, more volatile elements which give rise to process instability are less likely to be undesirably transported during electroslag remelting owing to the smothering effect of the slag and greater furnace pressure than in vacuum-arc remelting. Freckles can occur when lighter alloying elements rise through the solid-liquid region. This is more likely to occur during vacuum-arc remelting. The sulfur content of superalloys can also be minimized by electroslag remelting with fluxes having appreciable quantities of CaO.

This chapter summarizes electroslag remelting experiences with a number of superalloys.

NICKEL-BASE ALLOYS

With greater demand for materials that can withstand increasingly higher temperatures with improved strength, the search for alternate secondary-melting methods for nickel-base superalloys has intensified during the past several years. Electroslag remelting was a logical choice in this search, especially since strengths tend to decrease as ingot sizes and alloy contents increase. The electroslag process has demonstrated its effectiveness in the preparation of large ingots with enhanced properties and minimal segregation.

As mentioned in chapter 1, nickel-base superalloys have been electroslag remelted at Firth Sterling for a number of years. The process was particularly effective in preventing segregation in large billet sections of Inconel 718 because of

¹ Adapted in part from Cobalt, No. 4, December 1974, pp. 79-85, 91.

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shallow molten pools during melting. In addition, electroslag remelting, together with homogenization during forging, increased the strength and ductility of the alloy (13).

Soviet investigators have reported electroslag remelting of Monel metal without the hairline cracks and shrinkage porosity that presented a problem with other secondary-melting methods due to the alloy's wide range of crystallization (21). Up to 10 percent of the manganese was lost during melting; otherwise the chemistry remained unchanged. Other nickel-base superalloys have been electroslag-remelted in the Soviet Union with improved high-temperature ductility and impact strengths, as well as fewer inclusions as compared with air-melted material (24). However, alloy compositions were not specified.

Stellite Division of the Cabot Corp. has compared electroslag remelting with vacuum-induction melting and vacuum-arc melting for Udimet 700. High-temperature ductility was improved when homogenization heat-treatment techniques were optimized for material melted by the three processes, but electroslag remelting further improved hot ductility (15). At 2,000° F, electroslag-remelted material³ showed reductions in area of >50 percent, whereas material that was vacuum-arc-melted gave values of 30 percent as determined by Gleeble testing (16). Similar improvements were evident at other temperatures. However, subsequent work at Allvac failed to confirm these advantages for Inconel 901, as well as for Udimet 700 (8). Allvac investigators regard yield improvement as the major advantage of electroslag remelting over vacuum-arc melting. Further work at Stellite has demonstrated superior hot ductility of the same order of magnitude for ac-electroslag-remelted Hastelloy B and F over vacuum-arc-melted material (25). Fifteen-centimeter-diameter ingots were melted under CaF_2 - CaO - Al_2O_3 fluxes. Chemistry changes were minimal.

Over half of Stellite's electroslag production over the past 5 years has been the nickel-base superalloy Hastelloy X. A small gain in iron due to a mold wash and a slight decrease in silicon were the only impurity variations noted in ingots as a result of electroslag remelting. In addition, electroslag-derived wrought products had significantly fewer inclusions than vacuum-arc-melted products. For electroslag-remelted material subsequently rolled to sheet, over 400 specimens had 99 percent of their fields with

three or less thin type "D" globular oxide inclusions (ASTM-E45). This compares with 90 percent for the fields of 20 specimens of vacuum-arc-melted Hastelloy X. For bar products, the difference is more pronounced. In this case, over 500 specimens of electroslag-remelted material had 76 percent of the fields with three or less of these inclusions, whereas only 19 percent of the fields of 288 vacuum-arc-melted specimens showed comparable cleanliness. Electroslag-remelted products also possessed higher usable strength as determined from room temperature tensile tests, and had greater hot ductility (17). For example, at 2,300° F, a reduction in area of ~50 percent was obtained for vacuum-arc-melted Hastelloy X, whereas that for electroslag-remelted material was ~80 percent (7, 18).

Recently, the consumable melt shop at the Simonds Steel Division of the Wallace-Murray Corp. has been involved in electroslag remelting a variety of nickel-base superalloys (table 46). Electroslag-remelted porosity- and segregation-free ingots showed uniform composition in both transverse and longitudinal directions, with negligible compositional variation between the ladle analyses and the ingot (5). The worst field ratings for all types of nonmetallic inclusions in electroslag-remelted material were never greater than 1½ [ASTM-E45-63, modified JK chart, method D (1)] for any of the alloys. These results were comparable to those for vacuum-arc-melted material. Routine tensile and stress rupture testing demonstrated no significant differences between electroslag- and vacuum-arc-melted ingots of Inconel 600, 625, and 750. The major cited advantages of the electroslag process over vacuum-arc melting included an approximately 5 to 10 percent better yield, smooth ingot surfaces, and a more uniformly fine-grained structure (5).

René 41 and Udimet 700 have been successfully electroslag-remelted by Bhat (3). In both cases, ingot chemistry compared favorably with electrode chemistry, with 90 to 95 percent titanium and aluminum recoveries noted. Quaternary CaF_2 - CaO - MgO - Al_2O_3 fluxes were used (chapter 6) with both dc and ac power to melt 10- to 20-cm (~4- to 8-inch) diameter ingots and up to 28- by 50-cm (~11- by 20-inch) slabs. For René 41, room-temperature tensile properties of plate forged from 18-cm-diameter electroslag-remelted ingots were improved as a result of electroslag remelting, whereas tensile strengths at 1,700° F (927° C) were somewhat lower than

³ The flux used was 30 CaF_2 -17 CaO -13 MgO -40 Al_2O_3 , by weight.

those of electrode material, although hot ductility was improved. Excellent hot workability was demonstrated.

Recently, Klein (19) has demonstrated that electrosлаг-remelted hollow ingots of Hastelloy X and Inconel 718 (table 46) can be successfully prepared. The hollow ingots had a finer grained structure and less segregation than solid ingots of the same alloys. Wrought mechanical properties and microstructures were satisfactory. The elimination of several costly intermediate operations is an obvious advantage.

Elliott, Vorberger, Staton, and Mills (9) have recently reported on the advantages of ac electrosлаг remelting iron- and nickel-base superalloys solution strengthened with volatile elements. They used an ingot withdrawal technique and noted improved workability.

COBALT-BASE ALLOYS

In recent years, cobalt-base superalloys have become increasingly important for high-temperature structural materials, as well as for corrosion, oxidation, and sulfidation resistant applications. This is primarily the result of the more advanced nickel-base superalloy technology reaching its practical limit. Previous emphasis on nickel-base superalloys was due to the availability of nickel, better creep strength, and the advent of vacuum-arc-melting techniques to control aluminum and titanium which promote precipitation hardening in nickel alloys. Cobalt-base superalloys were found not to benefit as much from vacuum-melting techniques. Cobalt alloys, however, are reputed to possess longer high-temperature life and greater hot corrosion resistance (26).

Although considerable experience has been gained in electrosлаг remelting nickel-base superalloys, markedly less attention has been directed toward cobalt alloys. In addition, property comparisons for electrosлаг-remelted cobalt alloy material with other melting techniques are minimal (27).

Several wrought cobalt-base superalloys have been electrosлаг-remelted as reported in the literature. Sound electrosлаг-remelted 30-cm-square ingots of Haynes 25 alloy (10Ni-20Cr-15W-1.5Mn-0.5Si-0.1C-balance Co) have been used to produce sound 25-cm-diameter bars at CAFL in France (2). Sound ingots could not be produced from metal which was not electrosлаг remelted. In addition, ingots could be hot-forged without surface preparation. Paton, Medovar, and Latach (24) noted greater cleanliness and

generally greater hot ductility in electrosлаг-remelted cobalt-base alloys of unspecified compositions. Pridgeon, Pochon, Gross, and Sharma (25) concluded that electrosлаг remelting resulted in similar improvements as well as improved forgeability of two Haynes alloys, 6B (30Cr-4.5W-3Ni-3Fe-2Si-2Mn-1.5Mo-1.2C-bal. Co) and 31 (25Cr-10Ni-7.5W-1.5Fe-0.5Mn-0.5Si-0.5C-bal. Co), over vacuum-arc-melted material. Improved cold workability and higher tensile properties were also observed (11) for a relatively new electrosлаг-remelted low-chromium NASA alloy (VM-103: 25W-3Cr-1Ti-0.5Zr-0.5C-0.1Fe-bal. Co). Cook, Reese, and Gadsby (5) corroborated the improvement in hot workability for electrosлаг-remelted Haynes 25 (L-605, WF-11) alloy, which has also been electrosлаг-remelted by CAFL, Böhler in Austria, and Stellite (8). Stellite has also successfully electrosлаг-remelted Haynes 188 (22Cr-22Ni-14W-1.5Fe-0.08La-0.08C-bal. Co). All of the aforementioned improvements are probably related to greater solidification control in the electrosлаг process which can produce a more uniform and finer grain structure and more uniformly dispersed smaller inclusions.

In contrast to nickel-base alloys, cobalt superalloys rely chiefly on carbide and solid-solution strengthening, which means that easily oxidizable elements (such as aluminum and titanium) are less likely to be present. On the other hand, more volatile elements (such as manganese and nitrogen) which produce rough surfaces in vacuum-arc melting, are usually present. Therefore, the electrosлаг process should provide advantages for remelting cobalt superalloys. In addition, the columnar grain growth typically found in electrosлаг-remelted ingots might result in significant property improvements for cobalt alloys such as has been experienced with nickel-base superalloys. Stress-rupture properties and ductility are particularly dependent on grain orientation. Large-scale (greater than 61-cm-diameter) superalloy ingots melted by the electrosлаг process are possibly less susceptible to segregation than vacuum-arc-remelted ingots (12). This is attributed to shallower molten pools which are possible in electrosлаг remelting.

Experimental Work

Alloys Investigated

Three new-generation cast cobalt-base superalloys (MAR-M302, MAR-M509, and X-45) were selected for investigation by the Bureau of Mines. This selection was based on (1) obtaining

Table 46.—Nominal compositions of nickel-base superalloys known to have been remelted by the electroslag process¹

Weight-percent

Designation	Al	B	C	Cb	Co	Cr	Fe	Mn	Mo	Ni	Si	Ti	W	Zr	Other	Type ²	Ref.
AF2-IDA	4.6	0.015	0.35	([†])	10.0	12.0	0.5 (max)	0.1 (max)	3.0	Bal	0.1 (max)	3.0	6.0	0.10	1.5 Ta	P	6,13,15
Hastelloy B	([†])	([†])	.12 (max)	([†])	2.5 (max)	1.0 (max)	5.0	1.0	28.0	Bal	1.0 (max)	([†])	([†])	([†])	([†])	S	21
Hastelloy F	([†])	([†])	.05 (max)	2.1 (with Ta)	2.5 (max)	22.0	Bal	1.5	6.5	45.5	1.0 (max)	([†])	1.0 (max)	([†])	([†])	S	21
Hastelloy X	([†])	([†])	.10	([†])	1.5	22.0	18.5	.5	9.0	Bal	.5	([†])	.6	([†])	([†])	S	16
Inconel 600	.2	([†])	.04	([†])	([†])	15.8	7.2	.20	([†])	76.0	([†])	.15	([†])	([†])	([†])	S	4
Inconel 625	.2	([†])	.05	4.0	([†])	22.0	3.0	.15	9.0	Bal	.30	.2	([†])	([†])	([†])	S	4
Inconel 718	.4	([†])	.04	5.0	([†])	18.6	18.5	.20	3.1	Bal	.30	.9	([†])	([†])	([†])	P	4,12
Inconel 750	.8	([†])	.04	.9	([†])	15.0	6.8	.70	([†])	Bal	.30	2.5	([†])	([†])	([†])	P	4
Inconel 901	.25	0.015	.05	([†])	([†])	12.8	35.0	.48	5.7	43.0	.22	2.4	([†])	([†])	([†])	P	7
Monel	([†])	([†])	.30 (max)	([†])	([†])	([†])	2.50 (max)	2.00 (max)	([†])	63-70	.50 (max)	([†])	([†])	([†])	Bal Cu	S	17
Monel 400	([†])	([†])	.14	([†])	([†])	([†])	1.5	1.0	([†])	65.0	.1	([†])	([†])	([†])	Bal Cu	S	8
RA 333	([†])	([†])	.05	([†])	3.0	25.0	18.0	1.5	3.0	Bal	1.25	([†])	3.0	([†])	([†])	S	4
Rene 41	1.5	.01 (max)	.09	([†])	11.0	19.0	([†])	([†])	10.0	Bal	([†])	3.1	([†])	([†])	([†])	P	2
Udimet 700	4.25	.05 (max)	.15	([†])	18.5	15.0	1.0	([†])	5.2	Bal	([†])	3.5	([†])	([†])	([†])	P	2,13-14
Waspaloy B	1.4	.006	.07	([†])	13.5	19.5	2.0 (max)	.75 (max)	4.3	Bal	.75 (max)	3.0	([†])	.07	([†])	P	7

¹ In addition, Inconel 713, IN-100, Rene 77 and 95, Astroloy, and Rolls-Royce C-263 (precipitation strengthened), and Hastelloy C, C-276, G, S, Inconel 601 and 706 (solution strengthened) have been reported to have been melted by the electroslag process (20).

² P = precipitation strengthened; S = solution strengthened.

³ Not specified.

as wide a composition range as possible, (2) probable commercial acceptability, and (3) present availability.

Since MAR-M302 contains negligible nickel, it belongs to one of two groups as defined by Bungardt (4) in which there is a tendency for the face-centered cubic (fcc) β -cobalt lattice to transform to the hexagonal α -cobalt lattice during solidification. In the second group, to which the MAR-M509 and X-45 alloys belong, nickel contents are higher, this transformation does not occur, and β -cobalt is the stable phase.

Compositions of as-received material and melting ranges as determined by DTA experiments (see chapter 5) are given in table 47. Typically, electrode fluorine contents were <0.004 weight-percent (specific ion electrode method); hydrogen 1 to 5 ppm (hot extraction method); phosphorus <0.005 weight-percent (gravimetric method); oxygen 100 to 125 ppm for MAR-M509 and X-45, and 35 ppm for MAR-M302 (inert gas fusion method); and nitrogen 4 ppm (MAR-M509), 16 ppm (MAR-M302), and 635 ppm (X-45) (modified Kjeldahl method). Carbon and sulfur were determined by combustion methods, Ta by X-ray fluorescence, and Cr, Fe, Ni, and W by atomic absorption. The MAR-M302 and

MAR-M509 alloys were received as 5.7- and 8.6-cm (~ 2.2 - and 3.4-inch) diameter by 120- and 107-cm (47- and 42-inch) long billets, respectively. To obtain consumable electrodes of optimum size, the MAR-M509 billet was forged to approximately 5.7-cm (2.2-inch) diameter at 1,150° to 1,160° C and air-cooled. The X-45 alloy was received as cast bars, each 4.5 by 5.0 by 25.4 cm (1.8 by 2.0 by 10 inches). For optimum electrode length and analytical samples, cutting was accomplished with cutoff wheels (47A46-M7-BM29, Pacific Grinding Wheel Co.,⁴ or WA90KRA, Allison-Campbell⁴) for the MAR alloys, and with an electric discharge saw for the X-45 electrode material.

Fluxes

Three flux compositions in the system CaF_2 - CaO - Al_2O_3 were selected for electroslag remelting the cobalt alloys. These fluxes were chosen on the basis of liquidus temperatures, melting ranges, and physicochemical properties. Criteria for selecting fluxes are described in chapters 5, 6, and 7. The ternary compositions chosen included, in weight-percent, 65 CaF_2 -25 CaO -

⁴ Reference to specific manufacturers does not imply endorsement by the Bureau of Mines.

Table 47.—Compositions and properties of cobalt-base superalloy electrodes

Alloy	Composition, wt-pct (balance Co) ¹								
	B	C	Cr	Fe	Mn	Ni	S	Si	Ta
MAR-M302	ND	0.90 ±.05	21.3 ±.7	1.0 ±.4	ND	ND	<0.01	D	8.5 ±.3
MAR-M509 ²	E+	.56 ±.01	22.0 ±.9	.27 ±.01	E+	11.4 ±.1	<.005	D+	3.62 ±.05
X-45	E+	.25 ±.05	25.3 ±.1	.90 ±.05	C+	11.9 ±.4	.011 ±.002	B	ND
Alloy	Composition, wt-pct (bal Co)			Average hardness BHN ²	Melting range				
	Ti	W	Zr		°F		°C		
MAR-M302	ND	9.9 ±.3	F+	398±3	2,242-2,442		1,329-1,339		
MAR-M509 ²	D+	7.2 ±.2	C+	396±1	2,417-2,493		1,325-1,367		
X-45	ND	7.2 ±.2	ND	286±4	2,413-2,518		1,333-1,381		

¹ Average of 2 to 7 determinations; 1 standard deviation indicated. Spectrographic analyses, wt-pct:

B = 0.3–3

C+ = 0.1–1

D+ = 0.01–0.1

D = 0.003–0.03

E+ = 0.001–0.01

F+ = 0.0001–0.001

ND = not detected.

² 3,000-kg load, 10-mm steel ball; average of 8 determinations.

³ Forged material.

10Al₂O₃, 54CaF₂-29CaO-17Al₂O₃, and 40CaF₂-37CaO-23Al₂O₃. One quaternary composition (30CaF₂-15CaO-15MgO-40Al₂O₃) also served as a flux. Flux treatment is described in chapter 7.

Melting Parameters

All melts were conducted in a modified vacuum-arc furnace as described in chapter 7 with an 8.9-cm (3.5-inch) diameter water-cooled copper crucible. For comparison purposes, the alloys were double-vacuum-arc-remelted to conform with current standard practice. Only one electroslag melt was conducted for each ingot. Electroslag melts were made with single-phase ac power, whereas the double-vacuum-arc remelts were made with dc straight polarity (electrode negative) power. As the MAR alloys contain Ta, Ti, and/or Zr (table 47), all melts except one X-45 melt were conducted under 1/3 atm helium which was backfilled after the furnace had been pumped to approximately 6×10^{-2} torr. The one X-45 melt was performed in air. Approximately 600 to 700 grams of dry, solid flux was charged into the furnace for each electroslag melt. All vacuum-arc-remelted ingots were hot-topped to minimize shrink cavities. These melts were conducted for comparison purposes. Pertinent melting parameters are presented in table 48.

Selection and Preparation of Analytical and Mechanical Test Specimens

Comparison of electroslag- and vacuum-arc-remelted ingots was based on metallography, hardness, tensile strengths and ductility at room

and elevated temperatures, and stress-rupture data obtained by testing specimens machined from bars cut from each as-cast ingot.

None of the cast ingots could be cut by conventional sawing. Abrasive-wheel cutting using the aforementioned wheels proved feasible and resulted in a minimum loss of material and the maximum number of test specimens.

Because the specimens were to be tested in the as-cast condition, attention was given to cutting the ingots so that as many test bars as possible came from a similar geometrical location near the outside of each ingot. The bottom 10 cm (3.9 inch) of each ingot was cut off and sectioned longitudinally into two halves. Slightly oversize bars, 1.3 cm by 1.3 cm by 10 cm (0.5 by 0.5 by 3.9 inch), were cut longitudinally from the outer portion of one ingot half. From these bars, specimens for elevated-temperature tensile tests were machined with a 7.6- by 0.64-cm (3.0- by 0.25-inch) reduced section and button ends. From the outer portion of the other ingot half, slightly oversize bars, 1 cm by 1 cm by 9 cm (0.4 by 0.4 by 3.5 inch), were cut longitudinally. From these bars, specimens for room temperature and stress-rupture tests were machined with a 5- by 0.64-cm (2.0- by 0.25-inch) reduced section and threaded ends. Figure 90 shows the layout on the end of a ingot to be used as a guide for cutting the two sets of bars.

Machining of the hard as-cast material required special tungsten carbide tool bits. The reduced sections and threads were ground.

A few additional bars were cut from the outer

Table 48.—Cobalt-base superalloy melting parameters

Alloy	Flux ¹	Atm ²	Melt rate, kg min ⁻¹	Amperes	Volts	Kwhr	Energy consumption, (kwhr kg ⁻¹)
MAR-M302	VAR	6×10^{-2}	1.50	2,470	27	8.97	0.74
	65F/25/10	1/3, He	.91	2,800	30	12.72	1.20
	54F/29/17	1/3, He	1.33	2,900	29	9.63	.97
	40F/37/23	1/3, He	1.43	3,000	29	11.46	.92
	30F/15/15/40	1/3, He	1.81	3,000	29	9.74	.80
MAR-M509	VAR	5×10^{-2}	1.42	2,554	27	5.92	.80
	65F/25/10	1/3, He	.94	2,900	22	7.52	1.07
	40F/37/23	1/3, He	1.20	3,000	26	8.53	1.07
	30F/15/15/40	1/3, He	1.61	3,200	29	9.81	.93
X-45	VAR	4×10^{-2}	1.48	2,420	26	5.51	.71
	54F/29/17	1/3, He	1.08	3,100	28	11.25	1.26
	40F/37/23	1, Air	1.06	3,300	25	9.21	1.12
	30F/15/15/40	1/3, He	1.41	3,400	26	8.29	.91

¹ Flux notation follows that given by Duckworth and Hoyle (6). The first number followed by an F is CaF₂ in wt-pct, followed by CaO and Al₂O₃. The quaternary flux is 30CaF₂-15CaO-15 MgO-40Al₂O₃(wt-pct); VAR = vacuum-arc remelt, no flux.

² For VAR remelts, values given in torr; for electroslag melts, values given in atm.

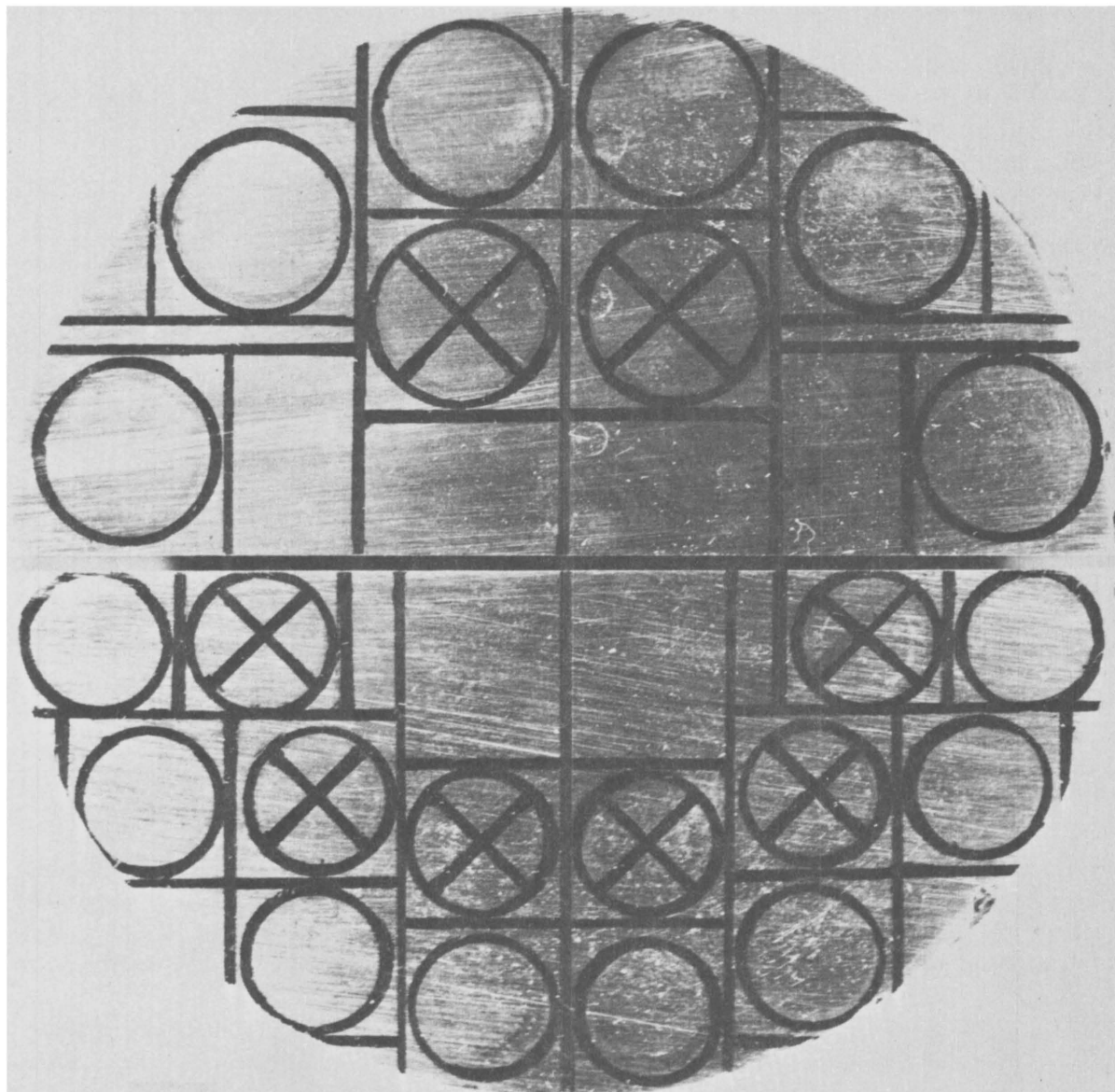


Figure 90.—Ingot cross-sectional layout used as a guide for cutting bars for tensile and stress-rupture tests. Outer bars with circles inscribed were machined into principal specimens, and those with x's inside the circles were used for "extra" specimens.

portion of the remainder of each half ingot to be used when it proved desirable to repeat a test. These specimens were identified as "extra" (X inside the circle in figure 90) and kept separate from the regular specimens obtained from the extreme outer portions of each ingot, until it was determined that there was no significant difference between the two groups. This care was thought advisable to minimize any variation in test data due to variation in cooling rates of the

as-cast material, depending upon its location in the ingot.

Specimens selected for transverse and longitudinal metallographic examination came from identical locations in each ingot, about 10 cm from the bottom and midradius. Specimens for gas analysis were obtained from the same location.

Analytical samples for chemistry of each ingot were obtained from turnings taken across the

face of the ingot at the 10-cm (3.9-inch) cutoff, along the 10-cm (3.9-inch) length of a machined tensile specimen, and from drillings from the top, middle, and bottom of the ingot.

Hardnesses were also obtained at identical locations in each of the ingots.

Mechanical Testing Procedures

Elevated-temperature tensile tests were conducted in air. The specimen was heated by its own resistance and was temperature-monitored and controlled by a platinum versus platinum-10 percent rhodium thermocouple spotwelded onto the test section. Tests were conducted at even 100° F intervals from 1,000° F (538° C) to 2,000° F (1,093° C) for the MAR-M302 and MAR-M509 alloys, and at odd 100° F intervals from 1,300° F (704° C) to 1,900° F (1,038° C) plus° F (316° C) and 1,000° F (538° C) for the X-45 alloy. Generally, only one specimen was tested at each temperature.

Room temperature tensile tests were conducted on a universal tensile test machine. Two specimens from each ingot were tested at room temperature. Strain rate for all tensile tests was 0.0254 cm/cm/min (0.01 in/in/min).

Stress-rupture tests were conducted in air with two standard machines enclosed in vertical tube furnaces. Two or more temperatures were chosen with a stress selected to result in rupture after 10 hours, and then after ~100 hours. Again, only one specimen was tested at each temperature and stress condition. The specimen was loaded inside a cold furnace and then brought to temperature. Heating time prior to stressing ranged from 1.5 to 6 hours. The specimen was then stressed at a predetermined load until rupture occurred. Temperature of the test section was monitored by three Alumel-Chromel thermocouples driving a recorder.

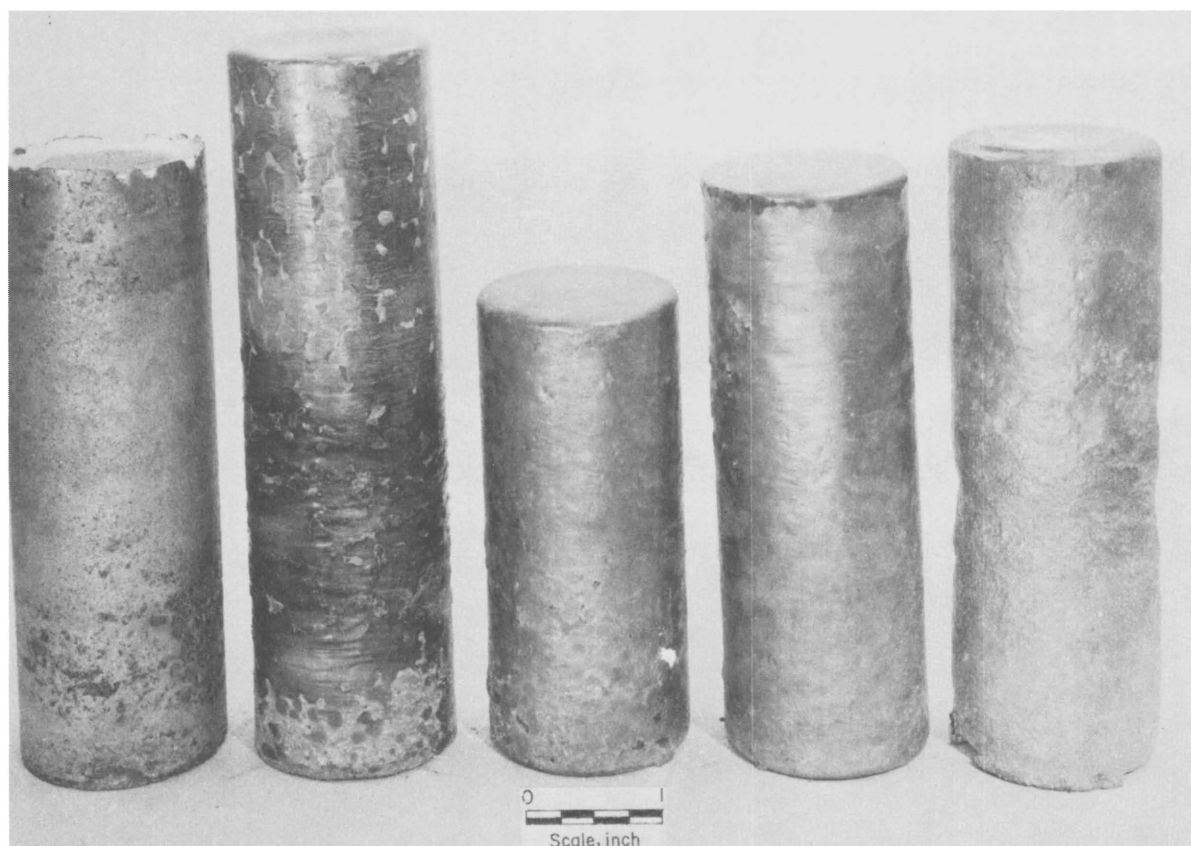


Figure 91.—Remelted MAR-M302 ingots. Vacuum-arc ingot on left, followed by electroslag ingots using the following fluxes as defined in table 48: 65F/25/10, 54F/29/17, 40F/37/23, and 30F/15/15/40.

Results and Discussions

Ingots

The three cobalt-base superalloys were successfully electroslag and vacuum-arc-remelted into 8.9-cm (3.5-inch) diameter ingots. Typical surfaces of a series of MAR-M302 ingots are shown in figure 91. The smoothest ingot surfaces were obtained on ingots melted with the ternary fluxes. Despite solid flux starting, excellent ingot bottoms were also obtained. Thick sidewall flux resulting from a small metal-flux liquidus temperature difference and a primary phase with an exceptionally high melting point ($\text{MgO} \cdot \text{Al}_2\text{O}_3$, $2,135^\circ \text{C}$) probably contributed to the relatively poor surfaces of ingots melted with the quaternary flux.

Ingot Brinell hardness values averaged 441 ± 12 for MAR-M302, 319 ± 5 for MAR-M509, and 275 ± 7 for X-45. There were no significant differences in hardness values between electroslag- and vacuum-arc-remelted ingots for each of the three alloys. Comparisons of ingot hardnesses with the electrode hardness values given in table 47 show an increase for MAR-M302 ingots and a decrease for MAR-M509; X-45 ingots remained approximately the same.

Each remelted ingot was cut longitudinally in

half, and the inside surface was etched with a 4:1 (by volume) concentrated HCl -30 percent H_2O_2 solution. Figure 92 illustrates typical macroetched sections. Noteworthy are the larger grain sizes in the ingot remelted with the quaternary flux and the tendency toward equiaxial grains in the center of the vacuum-arc-remelted ingot. This is probably the result of slower cooling rates in the ingot center, although this effect was not noted in electroslag-remelted ingots. The amount of equiaxial grains was in general inversely proportional to the CaF_2 content of the flux. Apparently the thermal conductivity of the flux is greater with increasing fluoride content and decreases with MgO additions, although specific data regarding this observation are not known.

Microstructure

Metallographic specimens were selected from each electrode and ingot. After mounting in Bakelite, these were ground and polished with $\frac{1}{4}$ -micrometer diamond and examined in the unetched condition. Representative photomicrographs are shown in figure 93. In the MAR-M302 samples, a face-centered cubic austenitic cobalt solid solution matrix (γ) is present. When the ternary CaF_2 - CaO - Al_2O_3 fluxes were used to

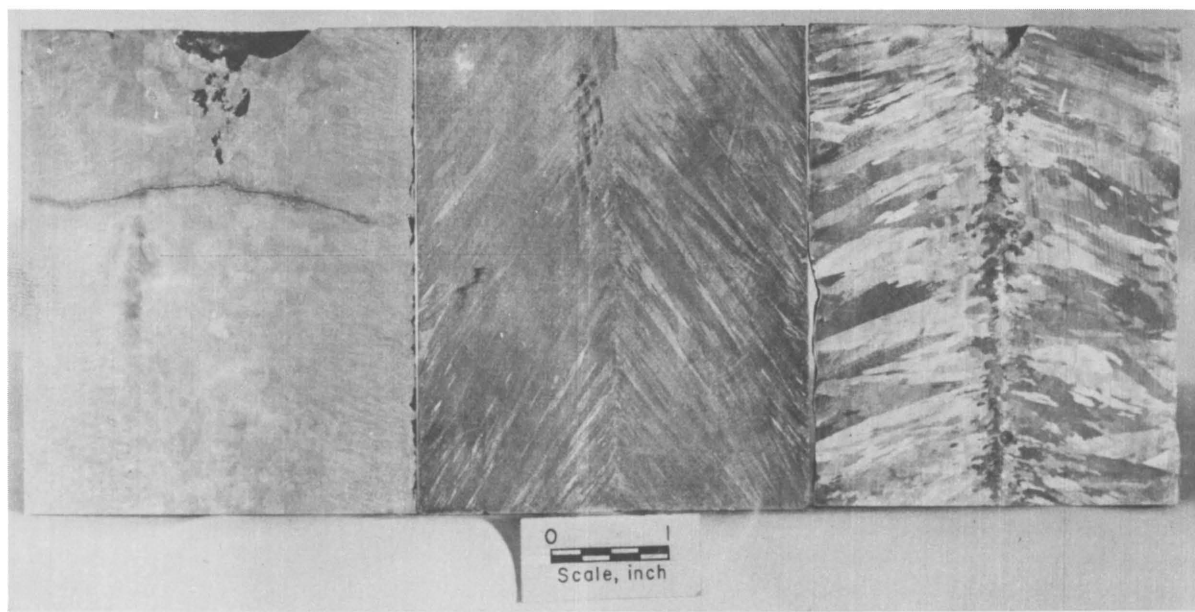


Figure 92.—Typical macroetched sections of top 10 cm (3.9 inches) of cobalt superalloy ingots. Left to right: MAR-M302, vacuum-arc-remelted ingot; MAR-M302, electroslag-remelted ingot, 65F/25/10 flux; MAR-M509, electroslag-remelted ingot, 30F/15/15/40 flux.

melt this alloy, the resulting ingots possessed a usually rimmed and blocky TaC phase with minimal Chinese-script morphology, which was predominant in the electrode material. However, the script carbide morphology was retained or increased when this alloy was either electroslag-remelted with the quaternary $\text{CaF}_2\text{-CaO-MgO-Al}_2\text{O}_3$ flux or vacuum-arc-remelted. The angular blocks are thought to precipitate first (24).

Somewhat larger lamellar eutectic islands of the M_{23}C_6 and M_6C phases are visible in samples of the ingots which were vacuum-arc-remelted and electroslag-remelted with the quaternary flux. No small secondary M_{23}C_6 particles were observed in any of the specimens from ingots melted with the ternary fluxes.

In the MAR-M509 forged electrode, the blocky TaC phase was concentrated at the grain boundaries and was more sparsely distributed than in the MAR-M302 electrode material. All MAR-M509 electroslag-remelted ingot samples were metallographically similar to those of MAR-M302 which were remelted with ternary fluxes. In vacuum-arc-remelted MAR-M509 ingots, however, the script carbide morphology predominated (fig. 93). The eutectic structure in MAR-M509 is composed of M_{23}C_6 and the fcc cobalt matrix. It is considerably less prevalent and more broken up than the eutectic phases in MAR-M302.

Since X-45 is lower in refractory elements and contains no tantalum, the MC phase is absent in this alloy. The eutectic phase (cobalt-matrix + M_{23}C_6) usually occurs at matrix grain boundaries and tends to coalesce in ingots remelted with the quaternary flux and by the vacuum-arc process. No small particles of secondary M_{23}C_6 were observed in any metallography specimens of this alloy.

Electron microprobe analyses were conducted on all as-polished metallographic samples to estimate phase compositions and variability. Phase compositions were uniform both within grains and from sample to sample of a given alloy, for cobalt and chromium in the MC phases. Typical phase analyses for each alloy are given in table 49. In the MAR-M302 alloy, there is no significant variation in phase composition as a function of melting parameters or flux compositions. There is a tendency for the cobalt and chromium to migrate from the matrix to the carbide phases, although the MC carbide in the vacuum-arc-remelted ingot is less impure than that phase in

electroslag-remelted ingots. Several oxide cluster inclusions were noted in the ingot remelted with the quaternary flux.

Constant phase compositions, regardless of melting history, characterize the MAR-M509 and X-45 ingots. Some migration of chromium from the matrix phases to the carbide and eutectic phases, as well as a loss of cobalt in the eutectic, was noted for MAR-M509 ingots during the remelting process. This also occurred in the X-45 ingots, where migration of chromium and possibly tungsten from the matrix to the eutectic phases occurred. The multiple phases which comprise the eutectic structure could not be differentiated by electron microprobe analyses in any of the alloys due to the very small grain sizes. Some irregular-shaped grains, which were high in iron and chromium, were observed in the X-45 specimens. Inclusions were particularly noticeable in electroslag-remelted X-45 ingot samples.

For each metallographic specimen representing all of the electrodes and as-cast ingots, the number of nonmetallic globular oxide inclusions were determined at X 100 and subsequently rated using ASTM Designation E45-63, Method D (1). Arithmetic mean values and the standard deviation were calculated for each specimen. These data permitted the computation of percentages of rated fields which were equal to or less than a given rating for each melt or series of melts, assuming a theoretical Poisson distribution. Worst-field ratings were also compiled for each specimen. The specimens were grouped according to similarities of important input parameters. The arithmetic mean and standard deviation of the ratings of each group were obtained, and the results were tested for significance using the procedure presented by Natrella (23) for comparing average performance. Other types of inclusion such as sulfides, alumina, and silicates were rarely observed in any of the material and hence were not amenable to this data treatment. The results are summarized in tables 50 and 51.

In terms of globular oxide inclusions, a significant improvement for electroslag-remelted material over vacuum-arc-remelted ingots is evident only for thin inclusions in MAR-M509. In all other cases, no significant improvement was noted. Both remelting processes reduce the number of these inclusions, with the exception of electroslag remelting X-45. Neither furnace atmosphere nor flux system is significant in re-

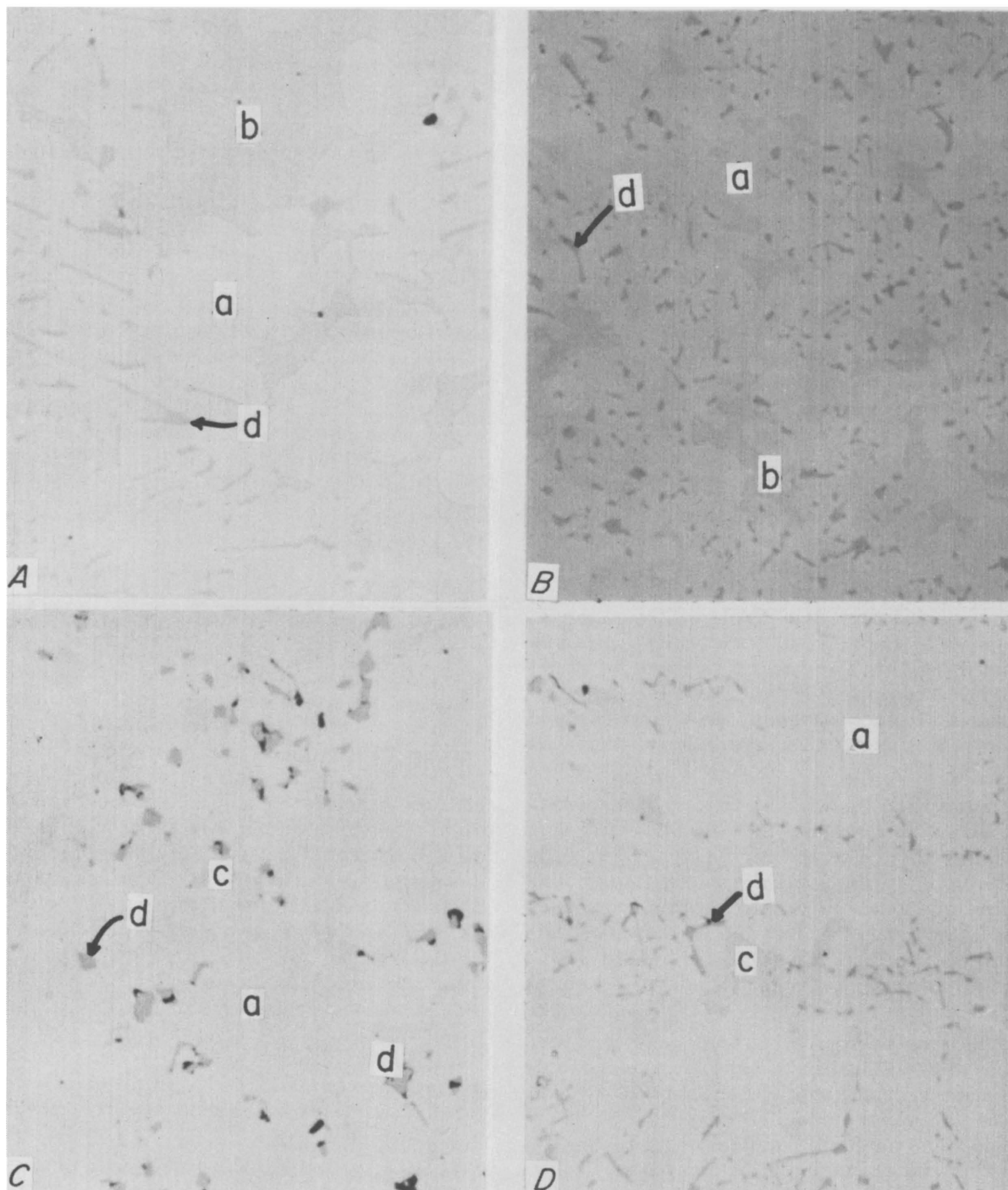


Figure 93.—Representative photomicrographs of cobalt-base superalloy electrode and remelted ingot specimens. Letters within panels key to phases as follows: a = cobalt matrix; b = $M_{23}C_6$ - M_6C eutectic; c = $M_{23}C_6$ -matrix eutectic; d = MC phase (M = metal). Individual panels are identified as follows:

A, MAR-M302, as-received electrode material, X 500; **B**, MAR-M302, electroslag remelted with $54CaF_2$ - $29CaO$ - $17Al_2O_3$ flux, X 500; **C**, MAR-M509, forged electrode material, X 500; **D**, MAR-M509, double-vacuum-arc-remelted ingot, X 500.

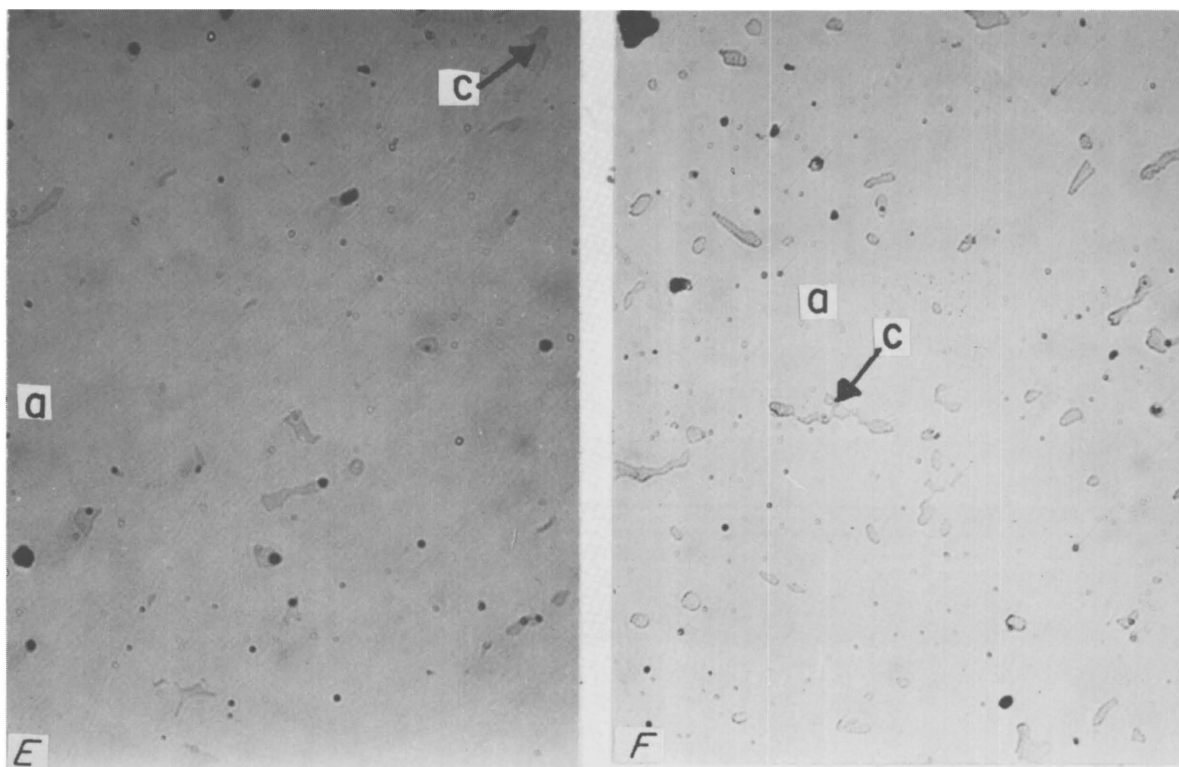


Figure 93.—Representative photomicrographs of cobalt-base superalloy electrode and remelted ingot specimen (Con.). Letters within panels key to phases as follows: A = cobalt matrix; C = $M_{23}C_6$ -matrix eutectic (M = metal). Individual panels are identified as follows:

E, X-45, as-received electrode material, X 250; *F*, X-45, electroslag remelted with 30CaF₂-15CaO-15MgO-40Al₂O₃ flux, X 250.

ducing the number of inclusions during electroslag remelting, except that CaF₂-CaO-Al₂O₃ fluxes appear to be more effective than the CaF₂-CaO-MgO-Al₂O₃ flux in the case of MAR-M302.

As stated in chapter 6, fluxes involving CaF₂, CaO, and Al₂O₃ are the most commonly used in the electroslag process. In many cases, these fluxes can produce nonmetallic inclusions in the ingot. Mitchell and Bell (22) have shown that fluorine is absent in inclusions present in electroslag-melted iron. Therefore, flux particles entrapped in the metal are not responsible for the presence of inclusions. In addition, no calcium is present in the inclusions, which precludes the presence of particles containing the flux primary solid phase from the sidewall flux. These authors concluded that ingot inclusions arise from chemical and electrochemical reactions with the flux and subsequent precipitation in the ingot. Typi-

cal reactions include (SiO₂) flux = [Si] + 2[O] = (SiO₂) incl. and (Al₂O₃) flux = 2[Al] + 3[O] = (Al₂O₃) incl. The solid-liquid metal interface is the probable nucleation and growth site for inclusions in the ingot metal. Ingot inclusions can also form as a result of low melting rates and shallow pool profiles which enhance inclusion flotation (14). Inclusions of all common compositions present in the electrode are generally believed to be rapidly dissolved when contact with the flux is made.

Chemistry

A summary of the analytical results for remelted ingots of the three cobalt-base superalloys and the oxyfluoride fluxes used is presented in table 52. Table 47 can be used for comparisons of ingot compositions with those of the electrode material for each alloy. Small amounts of chromium and nickel migrated from the metal into

Table 49.—Typical microprobe phase analyses in electroslag-remelted cobalt-base superalloys¹

Alloy	Co-matrix								Eutectic							MC carbide							
	Co	Cr	Fe	Mo	Ni	Ta	W	C	Co	Cr	Fe	Mo	Ni	Ta	W	C	Co	Cr	Fe	Ni	Ta	W	C
MAR-M302:																							
Electrode	66	27	2	ND	ND	1	7	<0.5	28	40	6	ND	ND	4	19	3	2	2	<0.5	ND	86	4	7
Ingot	64	25	1	ND	ND	2	6	.1	43	39	1	ND	ND	2	13	1	10	8	2	ND	79	3	4
MAR-M509:																							
Electrode	57	28	<.5	ND	11	1	6	<.5	48	33	<.5	ND	10	1	7	2	<10	<10	<.5	<5	>60	<10	<5
Ingot	58	25	.5	ND	12	1	5	<.1	34	43	~3	ND	9	2	9	2	14	5	<.5	2	63	1	6
X-45:																							
Electrode	53	30	1	0.5	12	ND	6	<.5	46	34	ND	1	10	ND	7	2	ND	ND	ND	ND	ND	ND	ND
Ingot	53	27	1	.3	13	ND	5	.1	28	42	1	2	11	ND	14	1	ND	ND	ND	ND	ND	ND	ND

ND = Not detected.

¹ Values represent the mean of approximately 3 separate analyses on each phase in each sample. Values obtained are within approximately ± 5 percent of the amount of element indicated.

Table 50.—Nonmetallic inclusion count analysis of cobalt-base superalloys

Alloy ¹	Total number of fields	Percent of fields $\leq$ indicated rating ²							
		D1/2T	D1/2H	D1T	D1H	D2T	D2H	D5T	D5H
MAR-M302:									
Electrode	46	0	9	2	22	29	65	94	100
ESR	116	50	78	81	98	91	99	100	100
VAR	25	28	72	84	100	100	100	100	100
MAR-M509:									
Electrode	70	1	63	13	100	49	100	93	100
ESR	83	10	28	45	87	81	100	100	100
VAR	26	0	19	8	100	62	100	100	100
X-45:									
Electrode	93	0	13	0	27	12	60	67	100
ESR	81	0	0	0	0	0	31	73	100
VAR	24	0	25	0	100	46	100	100	100

¹ ESR = electrosag remelted; VAR = vacuum-arc remelted.

² Refers to type D globular oxide inclusion with the ASTM E45-63 rating indicated (*I*). T = thin (diameter $\leq 8 \mu\text{m}$); H = heavy (diameter $\leq 12 \mu\text{m}$).

the flux during electrosag remelting, with the exception of chromium in MAR-M509. In all melts of this alloy, slight decreases in tungsten were noted. Increases in silicon were observed for both flux and metal in all melts. Sporadic losses of easily oxidizable elements such as titanium and zirconium also occurred.

In addition to the results involving the elements listed in tables 47 and 52, several other impurities were monitored. In all melts, both fluorine and hydrogen contents remained at <40

ppm and 1 to 3 ppm, respectively. Oxygen and nitrogen ranged from 16 to 34 ppm in all MAR-M302 and MAR-M509 electrodes and ingots. In X-45 material, however, oxygen contents ranged from 123 to 136 ppm in the electrodes to 22 to 89 ppm in the ingots. Nitrogen values for this alloy ranged from 560 to 647 ppm in both electrode and ingot material. These results are consistent with the greater incidence of nonmetallic inclusions noted in metallographic samples of X-45 (see table 50). Due to the flux compositions used, small amounts of aluminum and calcium transferred to the ingot metal during remelting. All electrode material contained a maximum of 0.01 weight-percent aluminum and 0.3 weight-percent calcium, whereas the corresponding ingots contained maxima of 0.3 weight-percent aluminum and 1 weight-percent calcium. Cobalt contents in fluxes ranged up to a maximum of 1 weight-percent after remelting. Electrode phosphorus averaged 15 ppm for all alloys. This usually decreased to <5 ppm in electrosag-remelted ingots.

All elements were within nominal compositions in as-received electrode material, for somewhat high nickel in MAR-M509 and X-45. The remelted ingots retained nominal composition ranges except that X-45 electrosag-remelted ingots tended to be low in chromium and nickel. Close control of alloy chemistry from electrode to ingot for both electrosag and vacuum-arc remelting processes has been demonstrated for all three cobalt superalloys studied. Considering the indicated uncertainties presented in tables 47 and 52, no significant differences between

Table 51.—Significance tests for grouped data of globular oxide inclusions in cobalt-base superalloys

Alloy	Test ¹	Significance ²		Significance level, pct
		Thin	Heavy	
MAR-M302 ...	X(SM)>X(ESR)	Yes	Yes	0.01
	X(SM)>X(VAR)	Yes	Yes	.01
	X(VAR)>X(ESR)	No	No	.05
	X(Tern)>X(Quat)	Yes	No	.01
MAR-M509 ...	X(VAR)>X(ESR)	Yes	No	.01
	X(Tern)>X(Quat)	No	No	.05
X-45	X(SM)>X(ESR)	—	No	.05
	X(SM)>X(VAR)	—	Yes	.01
	X(VAR)>X(ESR)	—	No	.05
	X(Air)>X(Inert)	—	No	.05
	X(Tern)>X(Quat)	—	No	.05

¹ Abbreviations are X = arithmetic mean; SM = electrode; ESR = electrosag remelted; VAR = vacuum-arc remelted; Tern = ternary electrosag fluxes; Quat = quaternary electrosag flux; Inert = backfilled, 1/3 atm helium used.

² Dash (—) signifies that exact inclusion ratings could not be obtained because the numbers of inclusion fell outside the ATSM ratings scale. This also applies to the comparison of electrode material with ESR and VAR ingots for MAR-M509.

Table 52.—*Elemental analyses of cobalt-base superalloy ingots and oxyfluoride fluxes*

Alloy	Composition, wt-pct (balance Co)										
	B	C	Cr	Fe	Ni	S	Si	Ta	Ti	W	Zr
MAR-M302:											
Nominal	0.01 (max.)	0.78- .93	20-23	1.5 (max.)	(¹)	(¹)	0.4 (max.)	8-10	(¹)	9-11	0.3 (max.)
ESR ingots ²	ND	.84 ±.01	20.2 ±.1	0.91 ±.02	C+	<0.005	C	8.8 ±.4	ND	9.5 ±.2	ND
Unused fluxes	F+	.017 ±.004	E+	E+	F+	.020 ±.008	C	ND	D+	ND	D+
Used fluxes	E+	.030 ±.004	C	F	ND	.087 ±.007	C+	A+	D+	ND	C+
VAR ingot ³	ND	.84 ±.04	20.1 ±.9	1.3 ±.5	B	<.005	C	9.2 ±.9	F+	9.5 ±.4	ND
MAR-M509:											
Nominal	0.01 (max.)	.55- .65	22.5- 24.25	1.5 (max.)	9-11	.015 (max.)	0.4 (max.)	3-4	0.35 (max.)	6.5- 7.5	0.6 (max.)
ESR ingots ⁴	ND	.59 ±.01	21.9 ±.01	0.31 ±.01	9.9 ±.2	<.005	C+	3.5 ±.1	D+	6.6 ±.2	F
Unused fluxes	F+	.018 ±.004	F+	D	F+	.020 ±.009	ND	ND	D+	ND	D+
Used fluxes	E+	.030 ±.008	C+	ND	D	.057 ±.003	A	A	C+	ND	C+
VAR ingot ³	ND	.59 ±.02	22.9 ±1.2	0.30	9.8 ±.3	.008 ±.003	C+	3.6 ±.1	D+	7.0 ±.1	ND
X-45:											
Nominal	0.015 (max.)	.25	25- 25.5	1-2	10- 10.5	(¹)	(¹)	(¹)	(¹)	7.0- 7.5	(¹)
ESR ingots ⁴	E	.23 ±.01	23.6 ±.5	0.99 ±.01	9.5 ±.2	<.005	B	ND	ND	7.7 ±.2	E
Unused fluxes	F+	.017 ±.004	F+	D	F+	.020 ±.009	C	ND	D+	ND	D+
Used fluxes	D	.050 ±.022	C+	ND	D	.116 ±.009	B	ND	D+	ND	E+
VAR ingot ³	E	.24	23.7 ±1.9	0.98 ±.01	9.5 ±.6	.008	B	ND	ND	7.9 ±.7	E+

ND Not detected.

¹ Not specified.² Average of top, middle, and bottom drillings, and turnings across the ingot face and along the length of a tensile bar of 4 ingots; 1 standard deviation indicated.³ Average of top, middle, and bottom drillings, and turnings across the ingot face and along the length of a tensile bar of 1 ingot; 1 standard deviation indicated.⁴ Average of top, middle, and bottom drillings, and turnings across the ingot face and along the length of a tensile bar of 3 ingots; 1 standard deviation indicated.

NOTE.—Flux analyses are averages of 4 compositions used for MAR-M302, and 3 for remaining alloys. Letters have the following meanings: A+ = 10-100, A = 3-30, B = 0.3-3, C+ = 0.1-1, C = 0.03-0.3, D+ = 0.01-1, D = 0.003-0.03, E+ = 0.001-0.01, E = 0.0003-0.003, F+ = 0.0001-0.001, and F = 0.00003-0.0003 wt-pct.

electrode and ingot compositions could be ascertained as a function of either flux composition, remelting process (electroslag or vacuum-arc), or furnace atmosphere ($\frac{1}{3}$ atm backfilled He, or air for X-45). The advantages of electroslag remelting MAR-M302, MAR-M509, and X-45 cobalt-base superalloys over more conventional processes therefore do not lie in the area of chemical refinement, with the possible exceptions of phosphorus and sulfur.

Mechanical Tests

Tensile test results at room and elevated temperatures of the as-cast electroslag-remelted material for each of the flux compositions used were similar, and therefore the data for each alloy were averaged and compared with the data for the vacuum-arc-remelted material representing that same alloy. Figures 94, 95, and 96 show these tensile test results for the three alloys. The

points on the curves representing electroslag-remelted material are the average of three to six values, and those on the curves representing vacuum-remelted material are usually for only one value.

Data were deemed valid from specimens that were obtained as "extra" test specimens to be used as needed where it was desirable to repeat tests. This was determined by comparing test results at room temperature for two of the "extra" specimens with those of the two regular specimens from the extreme outer portion of each of the five ingots of MAR-M302. No significant difference could be found between the two groups of specimens at the 90-percent confidence level.

A significant difference at the 90-percent level was found in the tensile and yield strength data as a result of the flux composition used in electroslag remelting, but it was not possible to determine this difference.

The tensile and yield strengths of the electroslag-remelted material are generally somewhat greater than those of the vacuum-arc remelted material in the case of the two MAR alloys. However, for the X-45 alloy, the tensile strength of the electroslag-remelted material is less than that of the vacuum-arc-remelted material, particularly below 800° C, but the yield strengths are nearly the same except at room temperature, where vacuum-arc-remelted material shows the greater strength. Ductility, as evidenced by percent elongation and percent reduction in area, is variable for ingots remelted by the two processes.

Thus, no real advantage of electroslag-remelted material over vacuum-arc-remelted material is found in strength or ductility properties.

The limited stress-rupture data for the electroslag-remelted material were combined, and a single curve was plotted by the least squares method for each alloy at each test temperature. These curves for each alloy were compared with those obtained from the test results from the vacuum-arc-remelted material for each alloy. The curves are shown in figures 97, 98, and 99 for the three alloys, respectively. The curves are drawn as straight lines, because the reference literature generally justifies this representation (28).

The electroslag-remelted MAR-M302 material at the three temperatures tested withstood approximately a 10 percent greater stress overall before rupture than the vacuum-arc-remelted material. Accordingly, the electroslag-remelted material withstood the same stress before rupture

for a 50 to 70 percent longer time than the vacuum-arc-remelted material.

For the MAR-M509 ingots, the electroslag-remelted material withstood only a slightly greater stress, but for approximately a 50 percent longer time than the vacuum-arc-remelted material at 816° C (1,500° F). However, at 1,093° C (2,000° F), there is a crossover of the two curves, and the vacuum-arc-remelted material stands out as considerably superior at the lower stress.

Again, for the X-45 ingots, the electroslag-remelted material withstood approximately a 10 percent greater stress overall than the vacuum-arc-remelted material at 760° C (1,400° F), or a 50 to 150 percent longer time before rupture. However, at 1,038° C (1,900° F), a crossover of the two curves also occurs, and the vacuum-arc-remelted material withstands about 10 percent greater stress overall than the electroslag-remelted material or about an 80 percent longer time before rupture at the lower stress level.

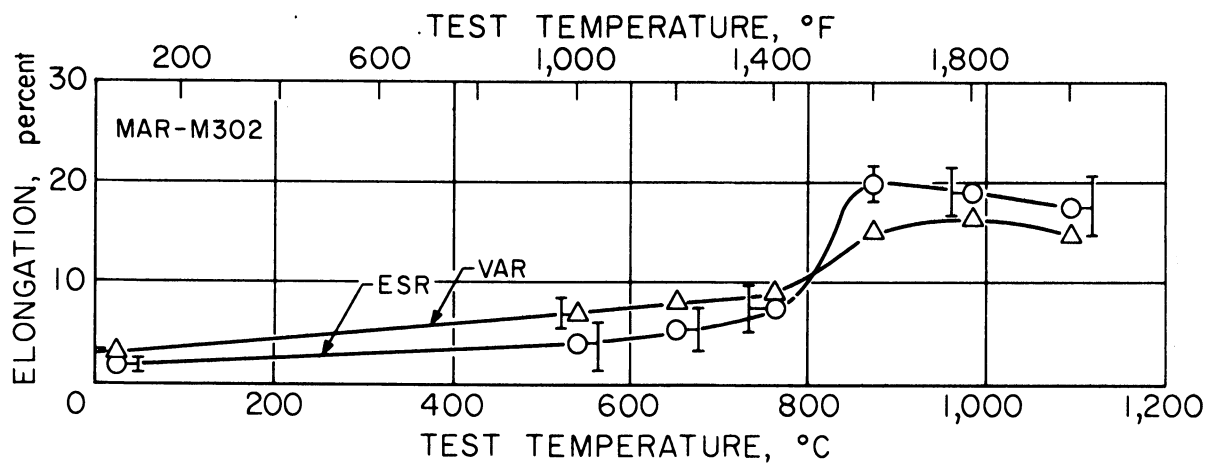
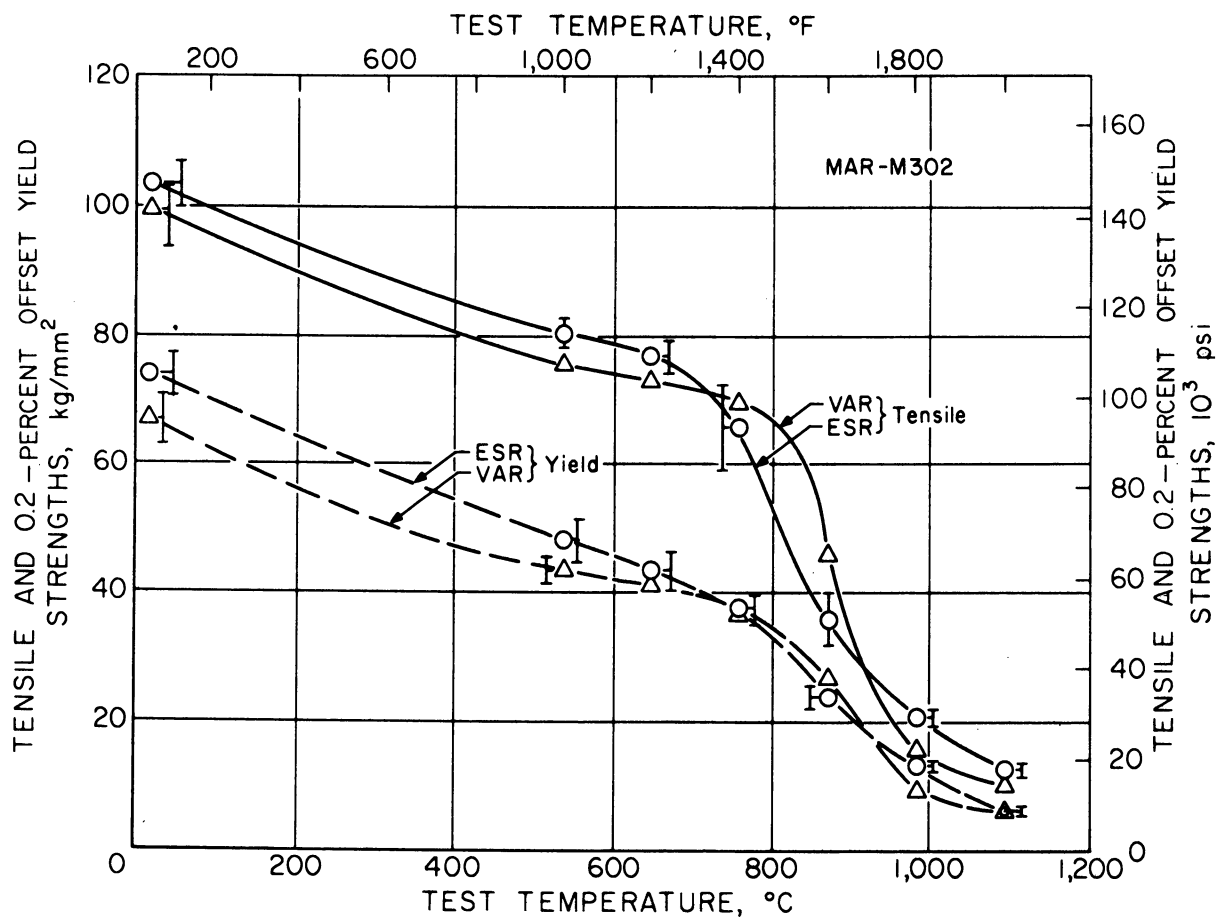
Thus, the stress rupture data indicate that ability to withstand stress is slightly greater overall for the electroslag-remelted material than for the vacuum-arc-remelted material, particularly at the higher stresses. However, the data are very limited, and these conclusions require cautious acceptance.

IRON-BASE ALLOYS

Iron-base superalloys that have been electroslag-remelted are tabulated in table 53. Firth Sterling has melted A-286 for a number of years with up to 17 percent titanium losses and an increase of aluminum due to Al_2O_3 in the flux (8). Electroslag melting improves ingot surfaces of this alloy because magnesium volatility leading to melting instability is suppressed. Experience in France has shown that titanium distribution was uniform throughout electroslag-remelted ingots, and yield was satisfactory, with improved hot ductility compared with the electrode material, according to Antoine, Jallas, Desolneux, and Boucher (2). Cook, Reese, and Gadsby (5) have demonstrated minimal nonmetallic inclusions in electroslag-remelted Inconel 902 and RA 330, and Garvey (10) commented on the favorable size capability and the sound Inconel 800 ingots prepared by the electroslag process.

ACKNOWLEDGEMENTS

We thank Wah Chang Albany Corp. for cutting the X-45 cobalt-base alloy on their electric discharge saw. Our thanks also go to R. R.



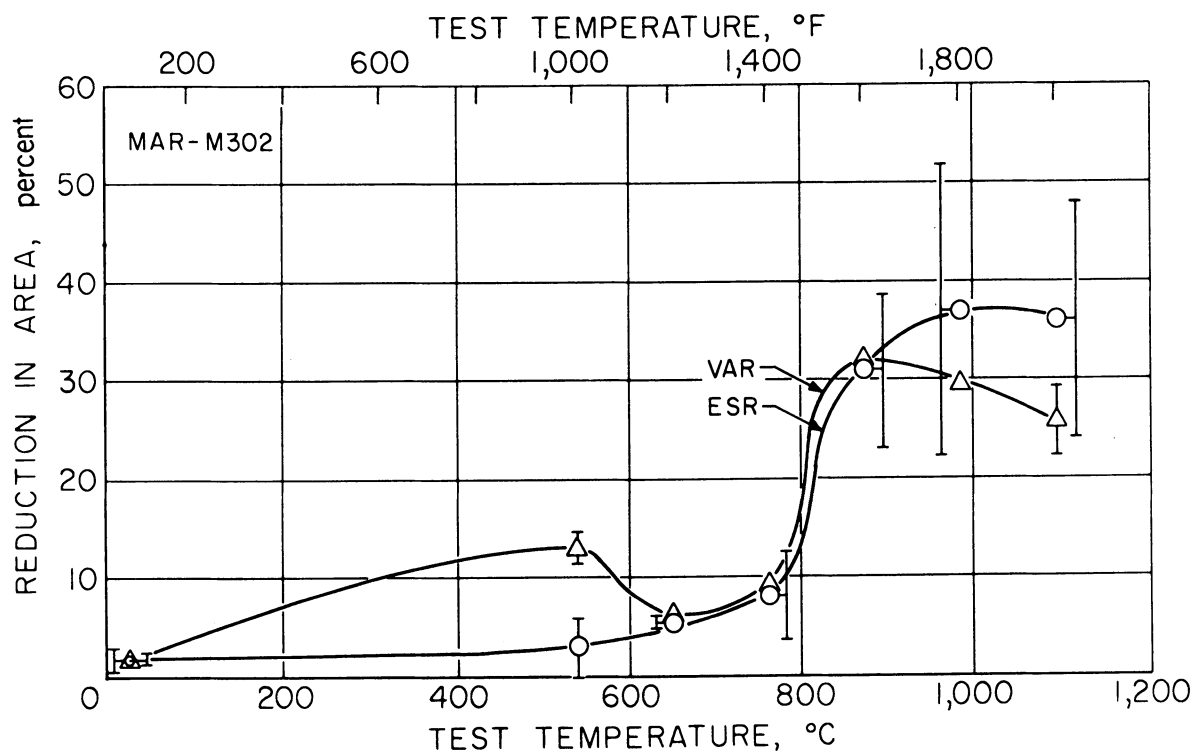
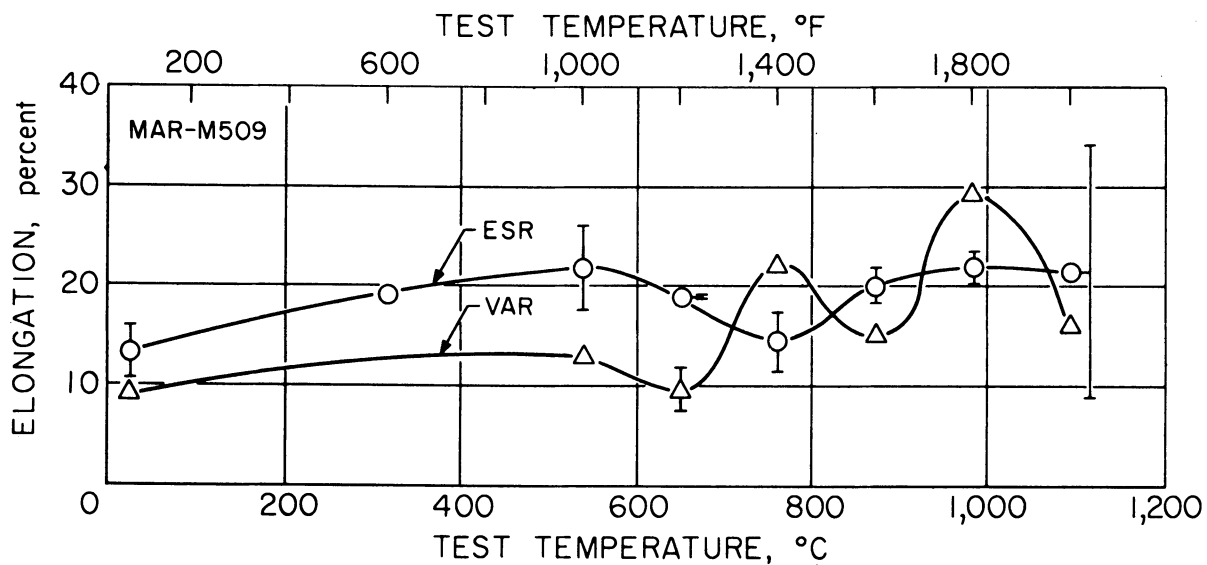
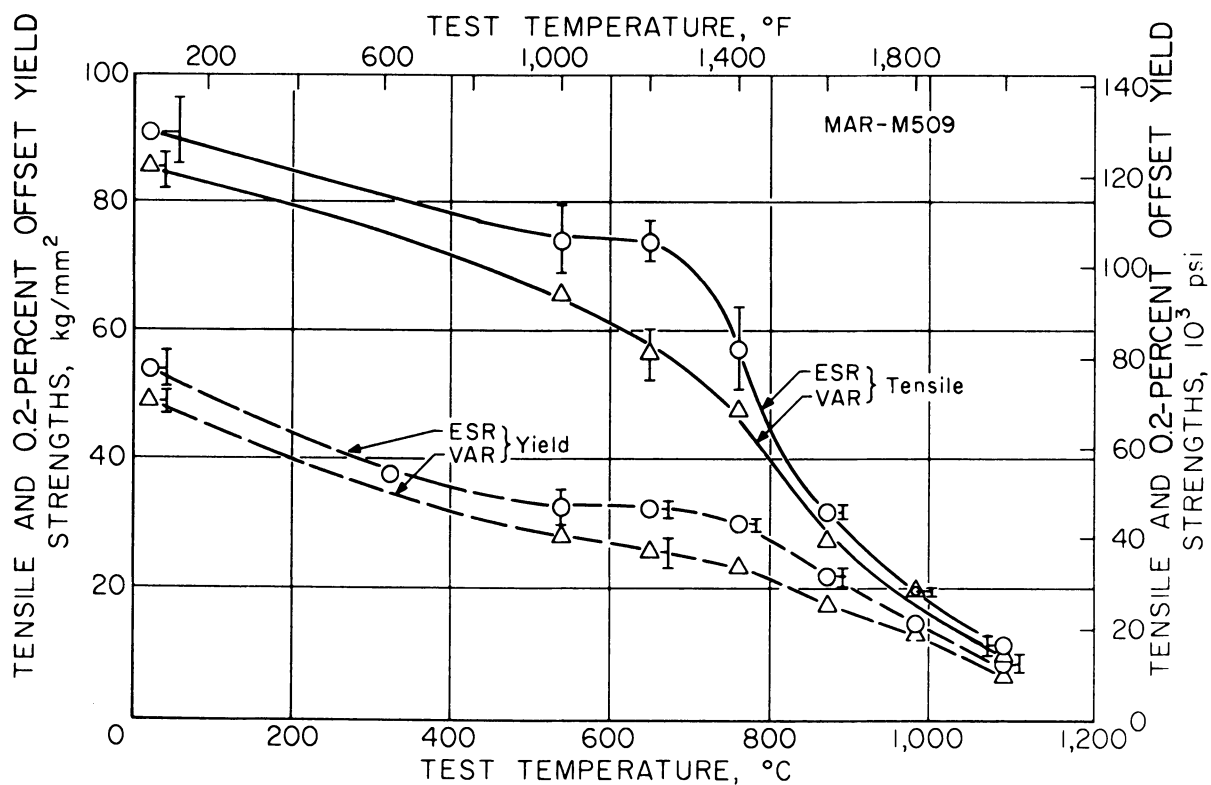


Figure 94.—Tensile properties of electroslag-remelted MAR-M302 cobalt alloy specimens compared with those of vacuum-arc-remelted material. Brackets indicate one standard deviation; where no bracket is indicated, the datum point represents one ingot specimen.



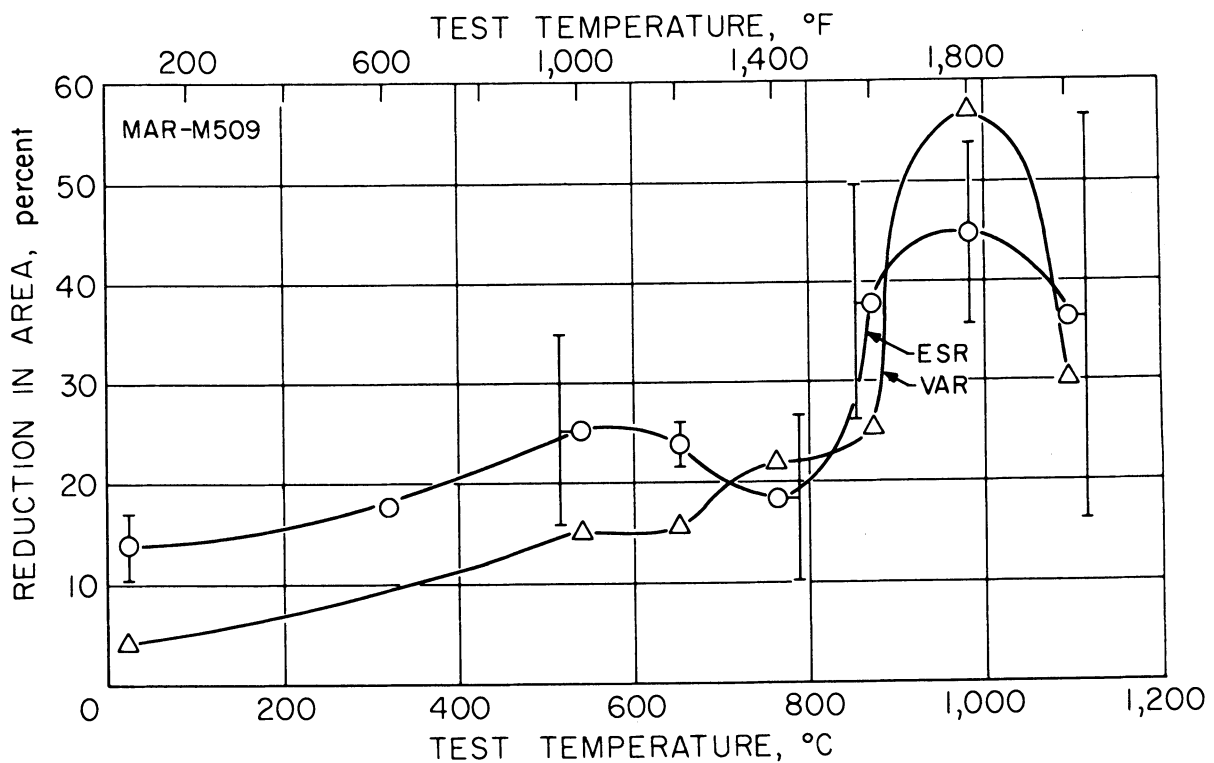
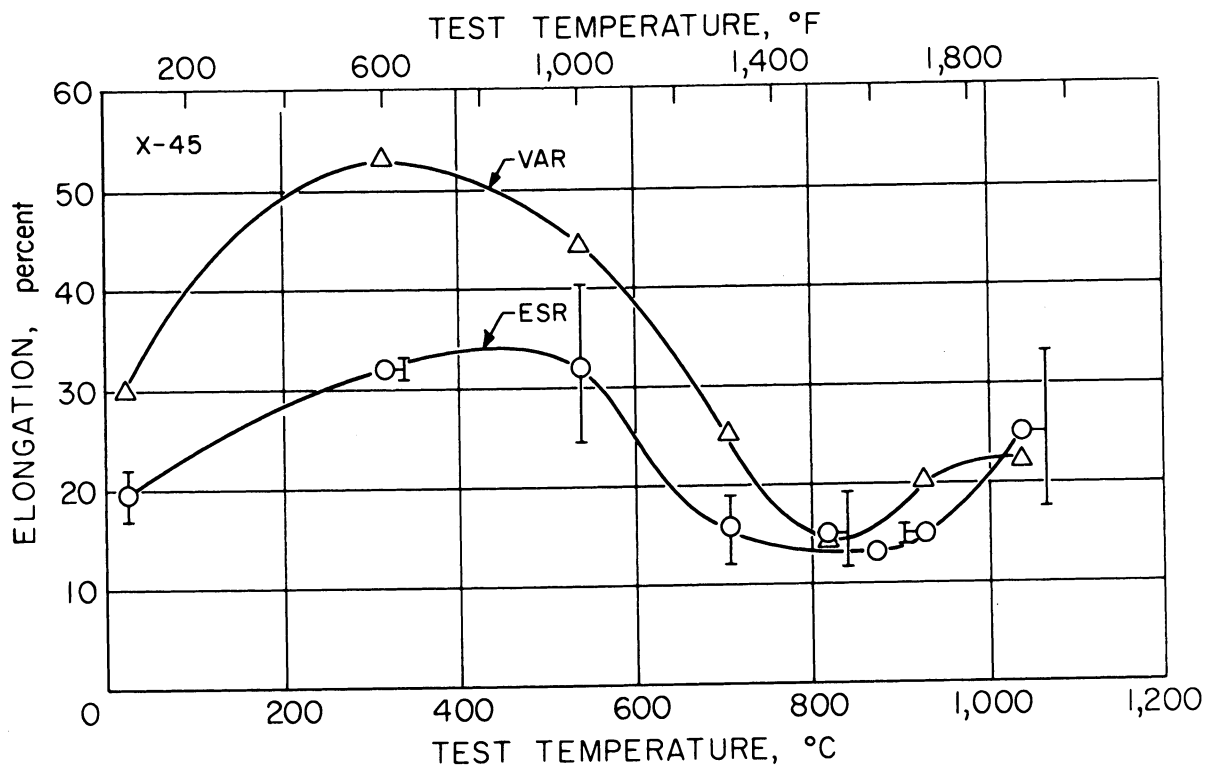
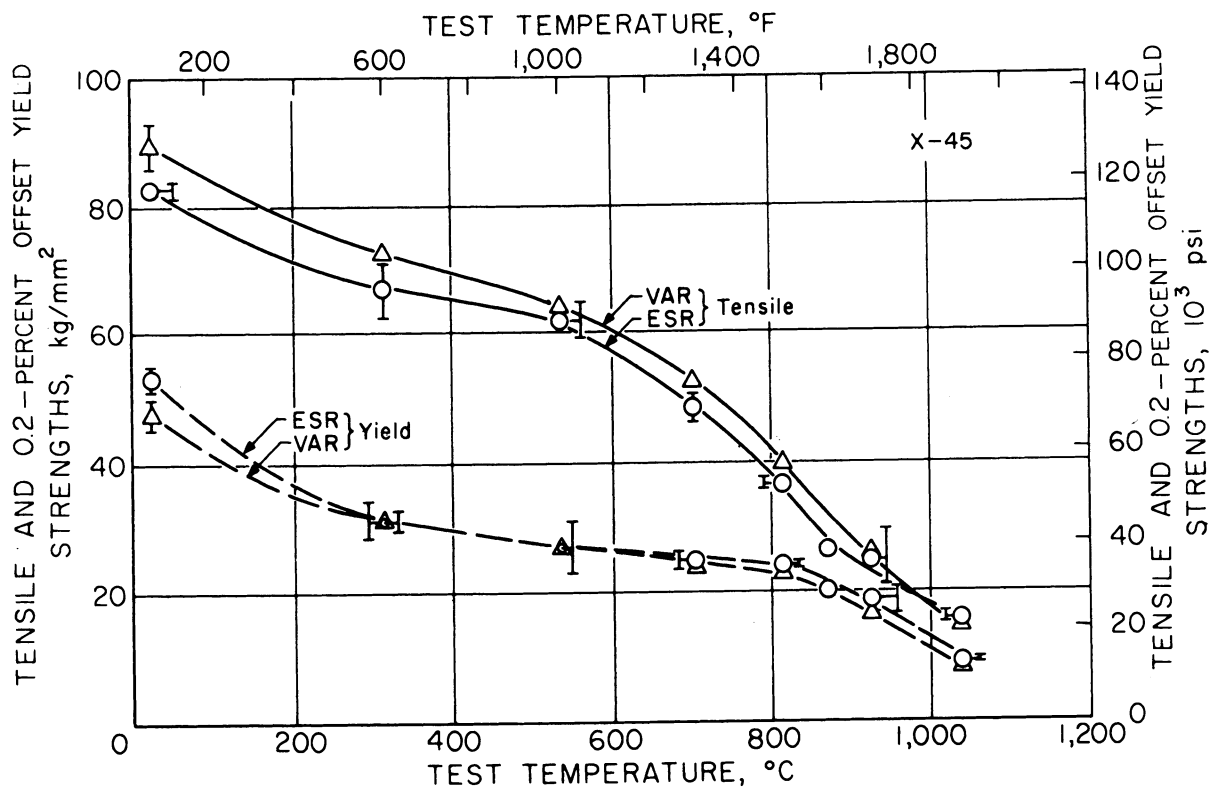


Figure 95.—Tensile properties of electroslag-remelted MAR-M509 cobalt alloy specimens compared with those of vacuum-arc-remelted material. Brackets indicate one standard deviation; where no bracket is indicated, the datum point represents one ingot specimen.



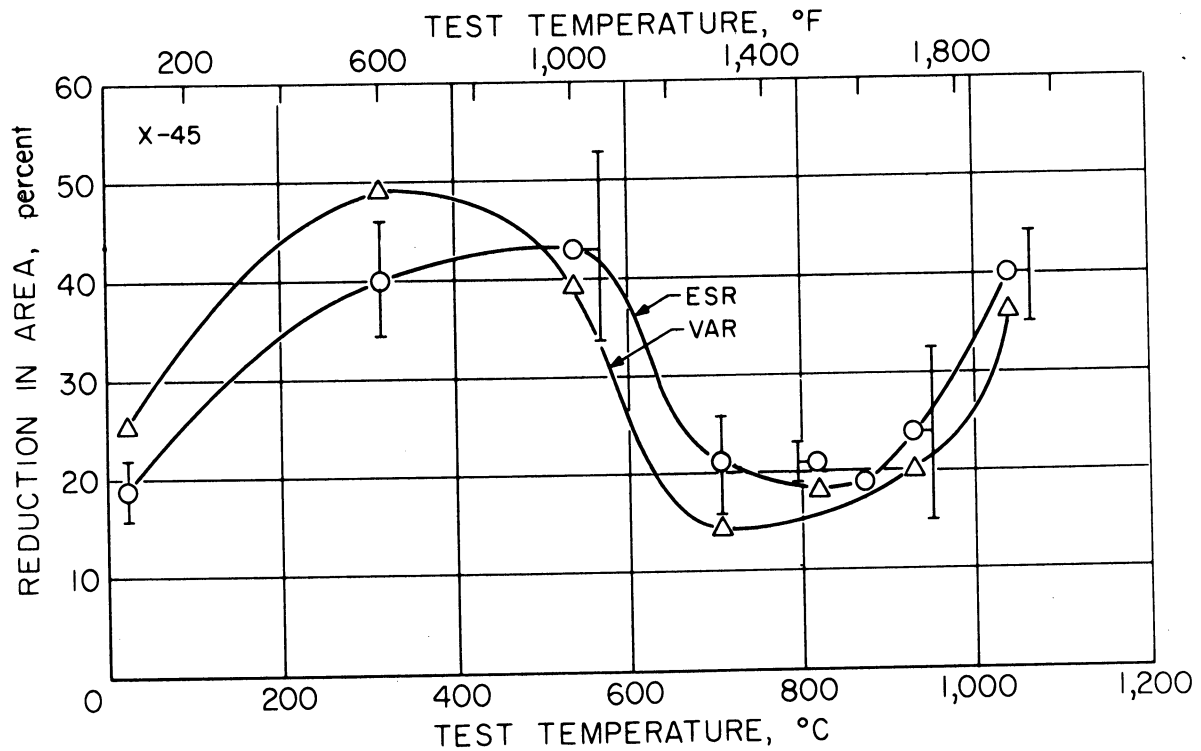


Figure 96.—Tensile properties of electroslag-remelted X-45 cobalt alloy compared with those of vacuum-arc remelted material. Brackets indicate one standard deviation; where no bracket is indicated, the datum point represents one ingot specimen.

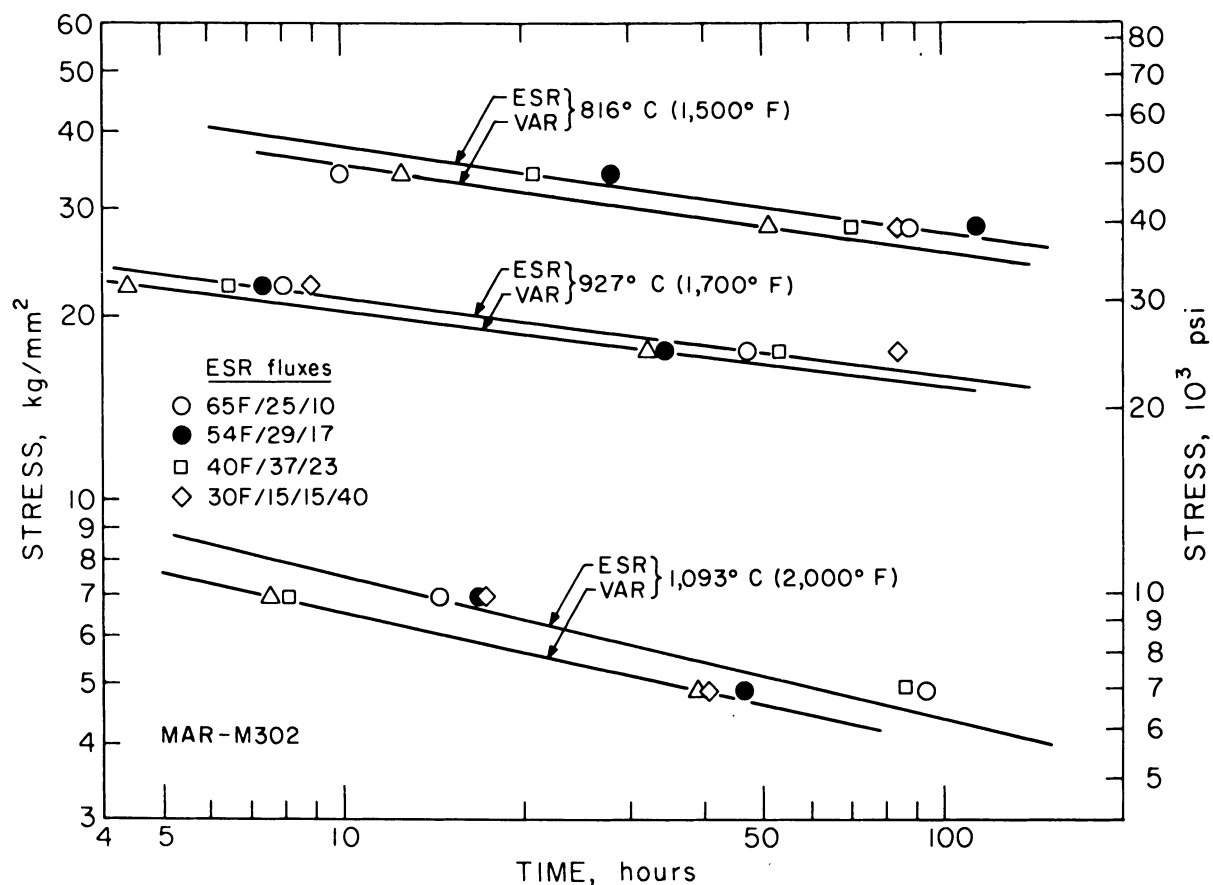


Figure 97.—Stress-rupture properties of electrosag-remelted MAR-M302 cobalt alloy compared with those of vacuum-arc-remelted material at three temperatures.

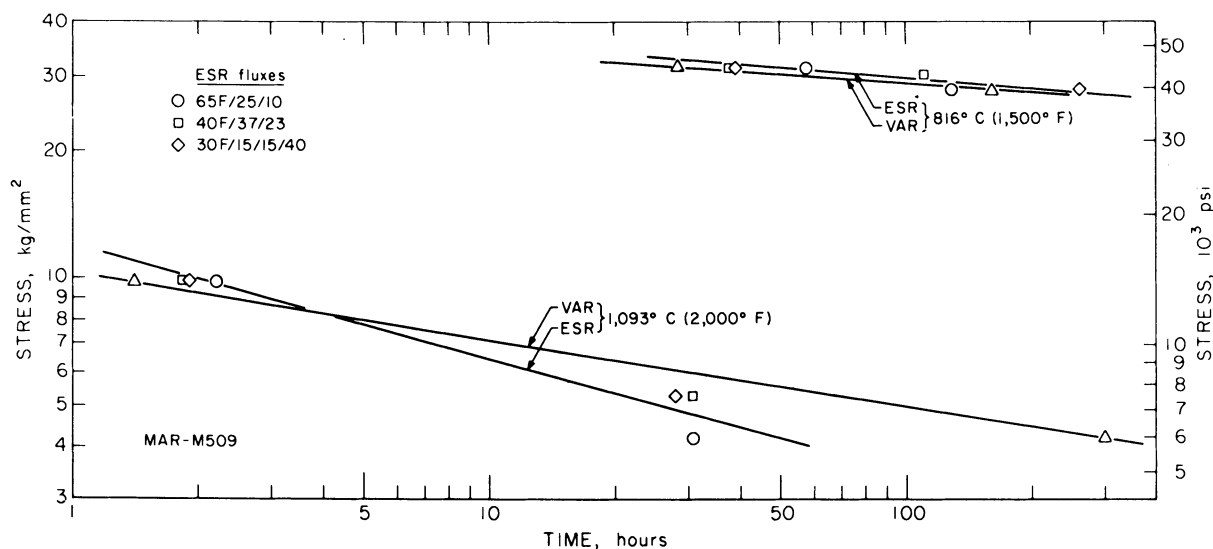


Figure 98.—Stress-rupture properties of electrosag-remelted MAR-M509 cobalt alloy compared with those of vacuum-arc-remelted material at two temperatures.

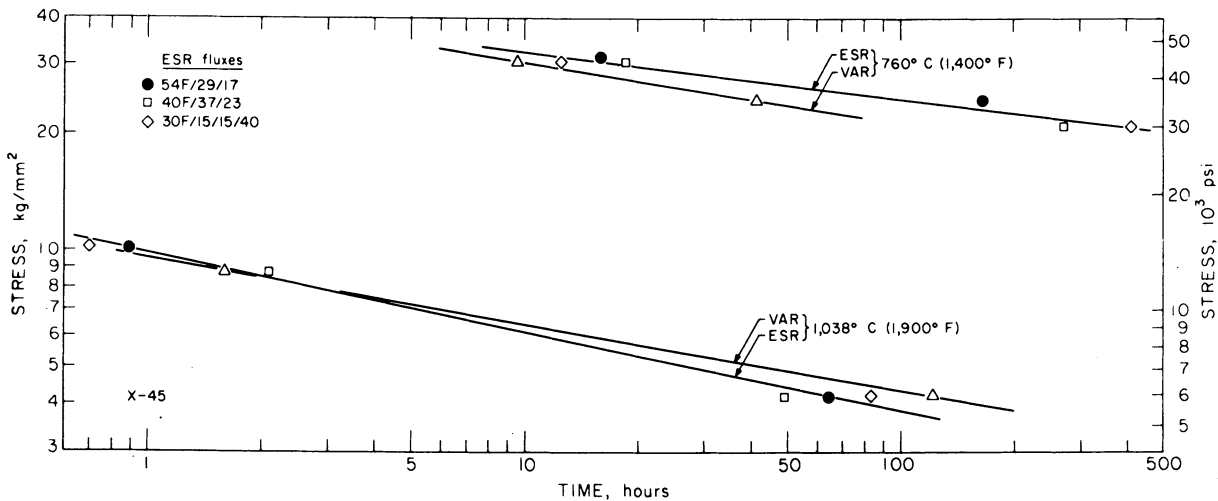


Figure 99.—Stress-rupture properties of electroslag-remelted X-45 cobalt alloy compared with those of vacuum-arc-remelted material at two temperatures.

Table 53.—Nominal compositions of iron-base superalloys that have been electroslag-remelted

Designation	Al	B	C	Cb	Co	Cr	Fe	Mn	Mo	Ni	Si	Ti	W	Other	Type ¹	Ref.
A-286	0.2	0.003	0.05	(²)	(²)	15	Bal	1.40	1.25	26.0	0.40	2.15	(²)	0.03 V	P	1, 7
Inconel 706	.4	.006	.06	2.9	1.0	16	Bal	.35	(²)	41.5	.35	1.75	(²)	.3 Cu	P	4
	(max.)	(max.)	(max.)		(max.)			(max.)			(max.)			(max.)		
Inconel 800	.38	(²)	.05	(²)	(²)	21	46	.75	(²)	32.5	.50	.38	(²)	(²)	(²)	8
Inconel 902	.70	(²)	.02	(²)	(²)	5.4	48.5	.40	(²)	42	(²)	2.4	(²)	(²)	P	4
N-155	(²)	(²)	.15	1.0	20	21	Bal	1.5	3.0	20	.5	(²)	2.5	.15 N	S	7
RA-330	(²)	(²)	.05	(²)	(²)	18.5	44	1.5	(²)	35	1.25	(²)	(²)	(²)	S	4
16-25-6	(²)	(²)	.08	(²)	(²)	16	Bal	1.35	6.0	25	.7	(²)	(²)	.15 N	S	7
			(max.)													

¹ P = precipitation strengthened; S = solution strengthened.

² Not specified.

Lowery and J. Sarvis of the Albany Metallurgy Research Center for performing the mechanical tests on the MAR-M302, MAR-M509, and X-45

cobalt-base alloys, and to H. Nielsen for conducting the statistical computations involving the inclusion counts.

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CHAPTER 15.—ELECTROSLAG-MELTED MOLYBDENUM ¹

By E. D. Calvert,² R. A. Beall,³ and H. Kato ⁴

The object of this work was to develop a molybdenum electroslag melting capability with the ultimate goal of preparing molybdenum ingots with improved yield from ingot to wrought product without adversely affecting the chemical or mechanical properties. The results of this investigation are encouraging; the stated goal was attained, and the electroslag ingots were readily fabricated to plate at temperatures lower than normally encountered for arc-cast ingots. Sheet rolled from this material appears to have properties superior to those of similar arc-cast material.

EXPERIMENTAL PROCEDURES

Equipment

A modified vacuum-arc-melting furnace of the type described in chapter 7 was used for electroslag melting molybdenum.

Materials

The molybdenum feed stock for this study was a commercial powder metal bar, pressed and sintered to a density of approximately 85 percent of theoretical. Typically, this material was at least 99.95 percent pure; the major impurities were oxygen and carbon.

Referring to desirable flux characteristics given in chapter 5, and considering the high melting point of molybdenum, it can be seen that the list of likely flux candidates is limited. Thermochemical calculations indicated that, of the few possible compounds, lanthanum oxide, yttrium oxide, and possibly beryllium oxide were best suited for our work. BeO was ruled out immediately because its use would require special facilities to safeguard personnel from toxic dusts. This left only La_2O_3 and Y_2O_3 . Theoretically,

La_2O_3 should have been superior to Y_2O_3 ; however, it was shown to hydrolyze in varying amounts to form $\text{La}(\text{OH})_3$. The presence of this compound caused gross, worm-hole-type porosity in the ingots prepared (an example of this is shown in figure 100); therefore, the use of La_2O_3 was precluded. This left Y_2O_3 as the sole remaining flux from the few possible choices.

The Y_2O_3 used was a highly refined powder with a total impurity content of less than 500 ppm. The major impurity was carbon, which was about 200 ppm. Prior to use, the powders were compacted and sintered or fused to densify and to remove sorbed gases and water. The compacts were then crushed and stored in closed metal containers in an oven held at 200° C until time of use.

Melting Practice

Usually the molybdenum electroslag heats were conducted with a backfill of approximately $\frac{1}{3}$ atm of helium gas after the system had been evacuated to a low pressure to remove atmospheric gases. On occasion, however, these heats were conducted with the valve to the vacuum pumps open while a constant stream of helium was added to maintain the system pressure at $\frac{1}{3}$ atm. Other melts were made under dynamic vacuum conditions without the addition of inert gases. The diversity of environmental pressure conditions was intended to explore the effects of this variable on melting ease and metal properties.

Because suitable equipment was not readily available for molten flux starts (see chapter 16), an alternative dry start method was used. It consisted of establishing dead-short conditions between electrodes, loading the total flux charge to completely fill the annular space between the electrode and crucible wall, and subsequently applying electrical power.

Without going into the details of heat transfer (see chapter 4), it should be noted that the pool shapes during arc melting and electroslag

¹ Adapted from J. Less-Common Metals, v. 23, 1971, pp. 129-151.

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⁴ Supervisory metallurgist, Albany Metallurgy Research Center (now deceased).

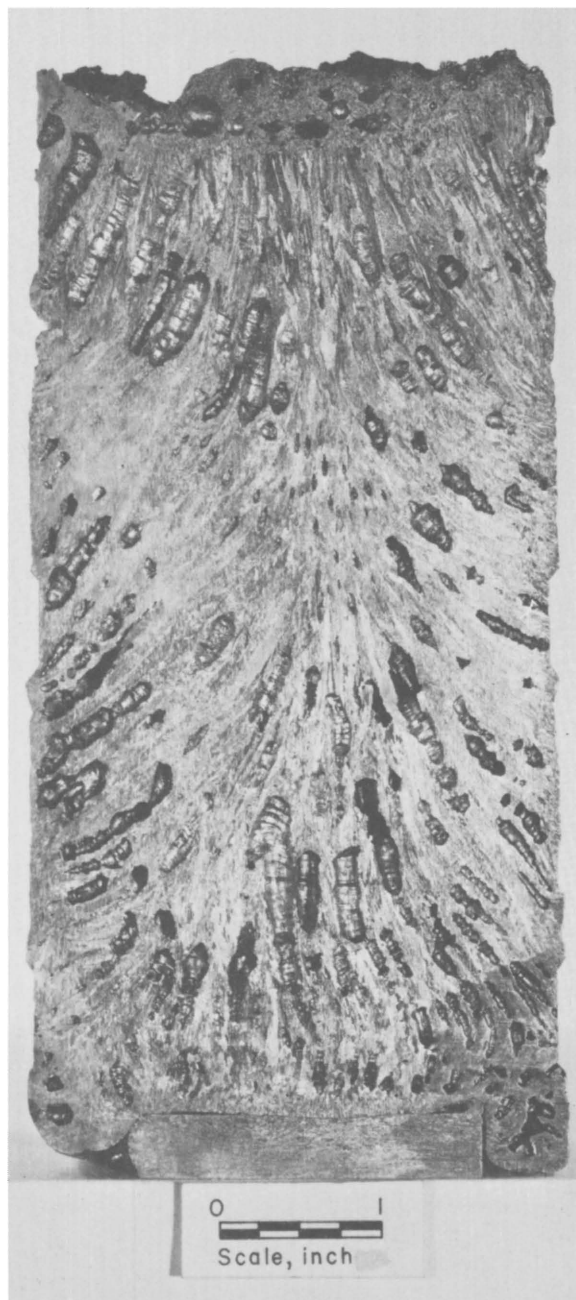


Figure 100.—Macrostructure of electroslag-melted molybdenum ingot prepared with La_2O_3 flux.

melting are very different. The arc-melt pool tends to be deep, whereas electroslag melting produces a broad, shallow pool. Because solidification and grain growth proceed normal to the liquid-solid interface, there is a difference in macrostructure orientation. These differences are

shown in figure 101. Vertically oriented columnar grains, some of which extend almost the full length of the ingot, characterize the electroslag melt. This is seen in figure 101 (left). The rolled appearance at the edge of the ingot resulted from change in melt rate. The broader portions indicate a higher heat input and a better filling of the pool.

To avoid porosity, prefused flux was found to be necessary. Variations in voltage (which are an indication of electrode spacing) and total power input seemed to be the major influencing parameters which determined ingot soundness, sidewall conditions, and yield.

When electrode-ingot spacing exceeds the slag depth, an arc to the top of the flux results. In this case, the melt rate is fast compared with the rate for melting with the electrode submerged at the same power. Shallow submersion of the electrode into the flux produces the best ingots if the flux depth is sufficient to effect good electrode spacing. However, this condition produces a much reduced melt rate and colder metal unless the melting current is raised sufficiently to compensate for the lower potential. If the current is not increased, the ingot surface tends to be somewhat rough. As the electrode and the ingot come into closer proximity, the characteristics of the resulting ingots become progressively worse. A satisfactory analysis of the changes in heating has not been made because data concerning the temperature gradient within the flux pool are not available. In fact, there is considerable doubt concerning the melting mechanism when the electrode is submerged in the flux. It is assumed to be a resistive heating mechanism in which the flux heats owing to its low electrical conductivity and causes the electrode to melt. The fact that the electrode is consumed more rapidly under conditions of reverse polarity may indicate that an arc exists in a highly ionized pocket immediately surrounding the electrode. Data to prove this are not available.

RESULTS

Molybdenum ingots 8.9 cm ($3\frac{1}{2}$ inches) in diameter were prepared by melting with a power input of 5,800 to 6,000 amperes at 18 to 24 volts. Typical melt rates were 0.68 kg min^{-1} ($1\frac{1}{2} \text{ lb min}^{-1}$). The variations in voltage determined the position of the consumable electrode with respect to the ingot and molten flux. At potentials higher than 22 volts, the mode of melting would often abruptly change from electroslag sub-

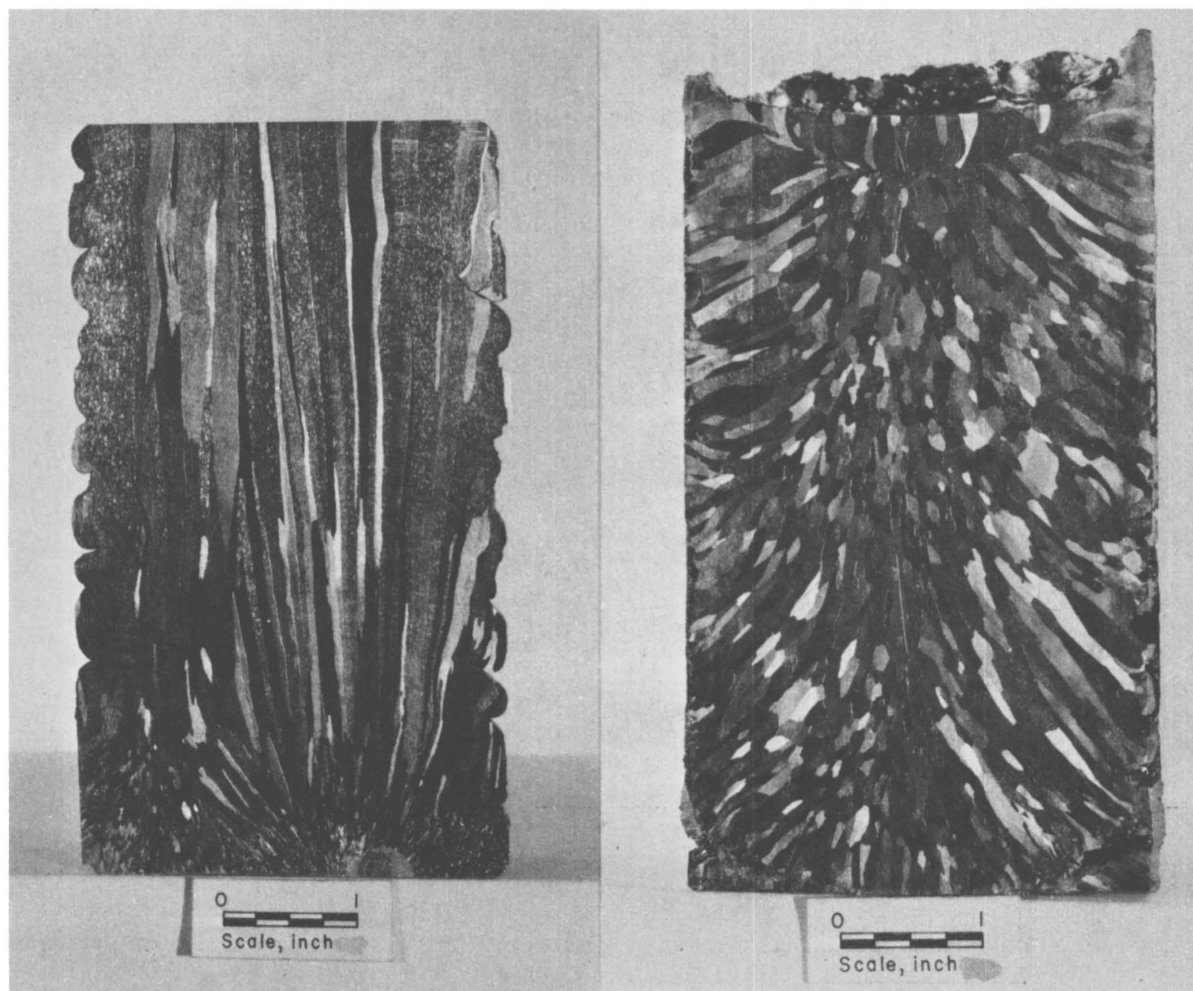


Figure 101.—Comparative macrostructures of electroslag (left) and arc-cast molybdenum ingots.

merged electrode to electroslag arc melting, and the melt rate would appreciably increase.

For purposes of comparison, a typical, once-melted electroslag ingot and a double-melted vacuum-arc ingot are shown in figure 102. The electroslag ingot is shown at the left. It is readily apparent from the smooth, lustrous appearance of this ingot that spatter and other agitations were absent in the area of the molten pool. Subsurface defects should therefore be minimal. Removal of the unfused starting pad and top surface dimple is sufficient to prepare an ingot of this sort for fabrication. On the other hand, the double-melted vacuum-arc cast ingot has extensive subsurface defects resulting from spatter and solidification faults in addition to a rela-

tively deep shrinkage cavity beneath the top surface.

Early metalworking experiments with electroslag-melted molybdenum ingots demonstrated that it was possible to successfully fabricate by upset forging at temperatures as low as 600° C. These low forging temperatures were without precedent in our experience. Ingot sections upset 50 percent, at temperatures ranging from 1,000° C downward to 600° C, are shown in figure 103. The optimum results appeared to have been obtained at about 700° to 750° C.

The level of oxygen in these ingots ranged upward to 300 ppm. Normally, molybdenum containing far less oxygen than this cannot be fabricated. In fact, we could not depend upon con-

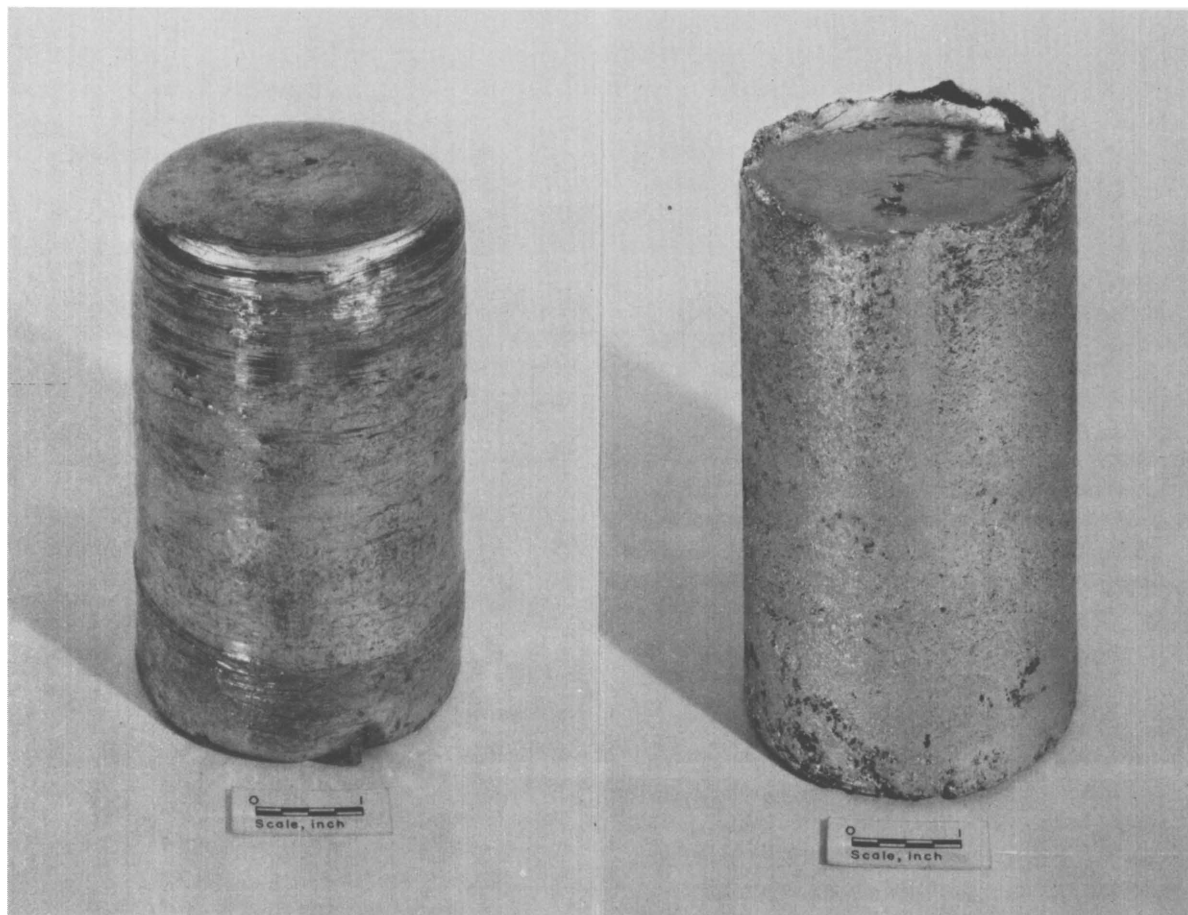


Figure 102.—Comparison of external surfaces of electroslog (left) and arc-cast molybdenum ingots in the as-cast condition.

sistent results. The reason for this apparently lay not only in the level of oxygen but in the way it occurred and how it was distributed. Comparative photomicrographs of two molybdenum structures, both produced by electroslog melting with Y_2O_3 and both with oxygen contents near 250 ppm, are shown in figure 104. Each contains extraneous grain-boundary phases which appear to be different. The ingot on the left was forged to a 50-percent reduction in thickness at $600^\circ C$. The other ingot could not be forged. The much greater etch-pit density of the lefthand structure is readily apparent. This could correspond to a higher surface energy, which in turn may be an indication of the termination of dislocations at the surface. Thus it is possible that pitting intensity is an index of a real dislocation density, according to F. W. Wood, Albany Metallurgy Research Center, Bureau of Mines.

Since there are uncertainties about the effect of the level of oxide contamination on the ductility of the product (some of the contamination is intergranular), it was felt necessary to hold the level of contamination to a minimum. Therefore attempts were made to reduce the level of contamination by varying flux chemistry and melting parameters. The reductants, carbon and yttrium were added to the flux, and various atmospheres, including vacuum conditions, were tried in attempts to reduce the oxygen content of the final ingot. In addition, electrode polarity was reversed to produce changes in heat distribution and ionic conditions. The effectiveness of these variables, singly and in combination, was evaluated with respect to oxygen content and fabricability of the final ingot.

Inert gas sweeps and vacuum, in combination with either straight or reverse polarity, were

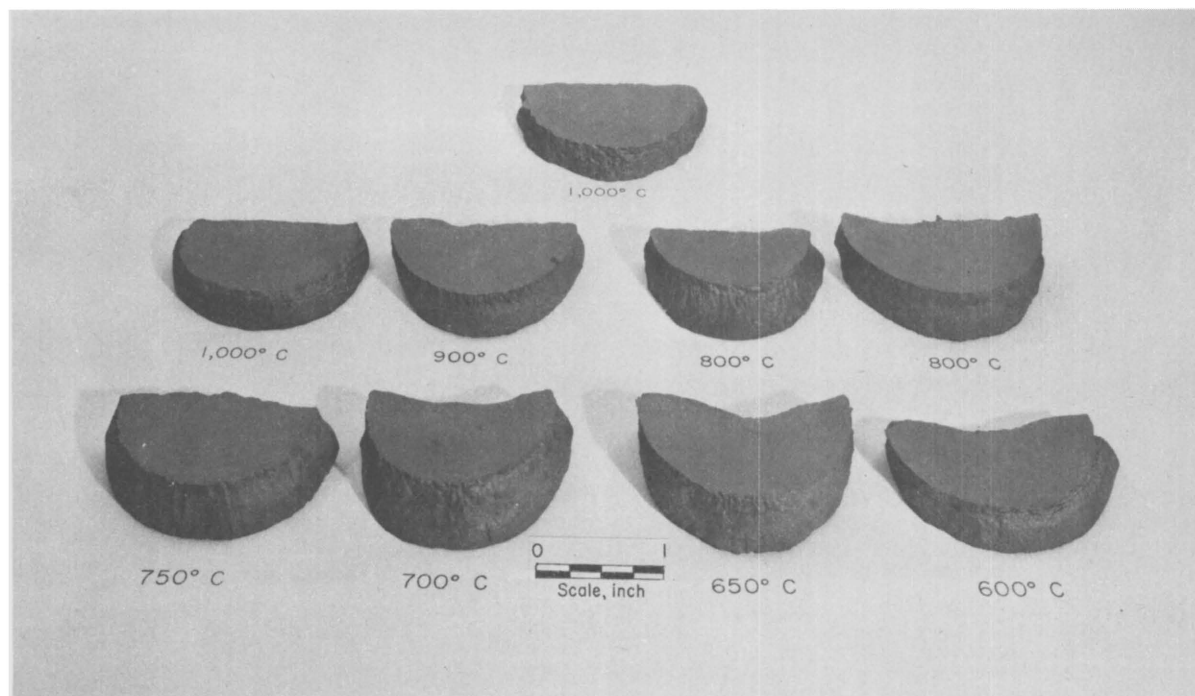


Figure 103.—Electroslag-cast molybdenum ingot sections press-forged at various temperatures.

found to be of only minor value unless a deoxidizer was also used. This was because the slag cover inhibits volatilization of vapors from the metal and MoO_2 probably decomposes too slowly to escape the molten pool before being trapped by freezing metal.

Both carbon and yttrium were successfully used to lower the oxygen level. Yttrium appeared to be a slightly better reductant than carbon. In combination with reverse polarity and dynamic vacuum, or helium-swept atmospheres, the oxygen level was lowered to levels ranging from 45 to 90 ppm by both additives to the flux.

Figure 105 shows typical microstructures of molybdenum melted with carbon and yttrium added as deoxidizers to the flux. The carbon-treated ingot microstructure appears on the left. It contained almost 16 ppm oxygen and nearly 700 ppm yttrium. The ingot deoxidized or treated with yttrium, on the other hand, contained less than 300 ppm yttrium; the precise level is unknown because this is the lower limit of detection by the analytical method employed. The oxygen level was reported as being 49 ppm and the carbon level, 13 ppm; this is lower than the carbon level reported in the melt stock. No significantly different structures appear to have

resulted from use of the different deoxidizers; both have relatively clean boundaries, and both show an indication of active areas within the grain. These are evidenced by the freckles of small spheroidal segregates. The seemingly rough appearance of grains in the carbon-treated microstructure probably represents worked metal resulting from specimen preparation.

The benefits derived from changes in electrode polarity are questionable, and when balanced against their influence on ingot yield, it is doubtful whether the use of reversed polarity can be justified, even though a somewhat lower oxygen content results.

A lower yield resulting from poor incorporation of the ingot bottom for reverse-polarity-melted ingots is normal. In addition, wall surfaces are significantly rougher than are the walls of ingots prepared by straight-polarity melting. These characteristics result from the changes in heat distribution. The anode receives more heat; therefore a faster melt rate results from reverse polarity (electrode anodic) melting, but the result is poorer ingot consolidation. This condition, previously mentioned, suggests that heating of the electrode cannot be entirely due to the electrical resistance of the flux. Alternatively,

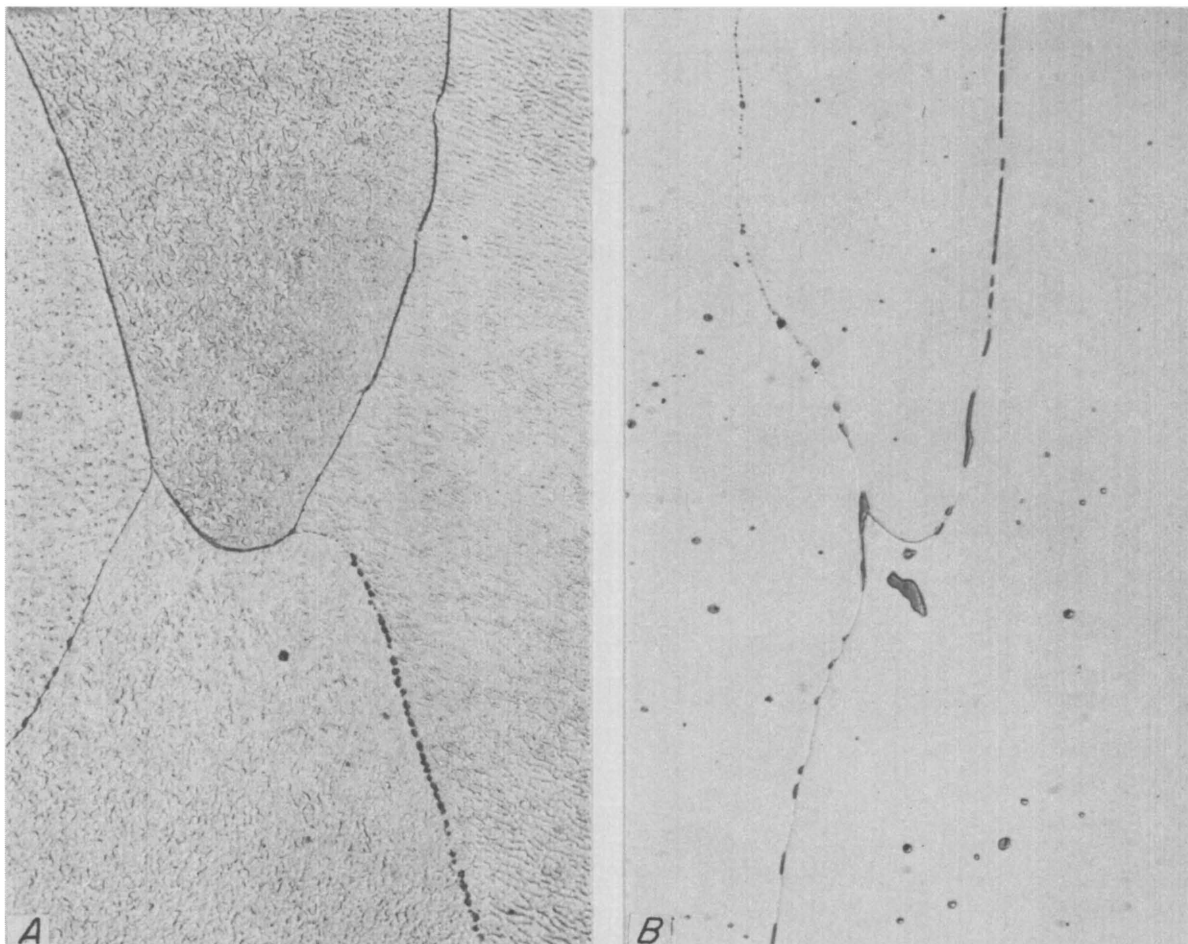


Figure 104.—Comparative photomicrographs of electroslag molybdenum structures illustrating a difference in second-phase grain boundary constituents, as-cast condition, X 250.

electrochemical effects could produce the same phenomenon.

The level of carbon and yttrium in the ingots was raised as a result of the use of these elements as deoxidizers. Their form, whether complexes, compounds, or free elements, is not known, nor is the extent of their influence upon fabricability. Carbon was detected at levels ranging from a little over 100 ppm downward to about 10 ppm, and yttrium ranged from about 750 ppm down to the lowest limit of analytical detection at our laboratory. It is interesting to note that the ingot with the highest yttrium level resulted from deoxidation with carbon, not yttrium.

FABRICATION

Because a large portion of the arc-cast molybdenum produced is ultimately used as a

wrought product, the value of any new process must be based, in part, on the working characteristics of the metal produced. During small-scale forging tests electroslag-melted ingots were encountered that could be worked as low as 600° C. This is well below the recrystallization temperature and just barely above the temperature where oxidation becomes a consideration.

The fabrication program was based on a schedule of forging at temperatures well below those normally used during primary fabrication. Secondary fabrication by rolling was performed at more conventional temperatures. The 8.9-cm (3½-inch) diameter evaluation ingots, which had been produced with and without deoxidizers added to the Y_2O_3 flux, were upset-forged and side-forged on a 454-metric-ton (500-ton, British Units) press at approximately 500° C.

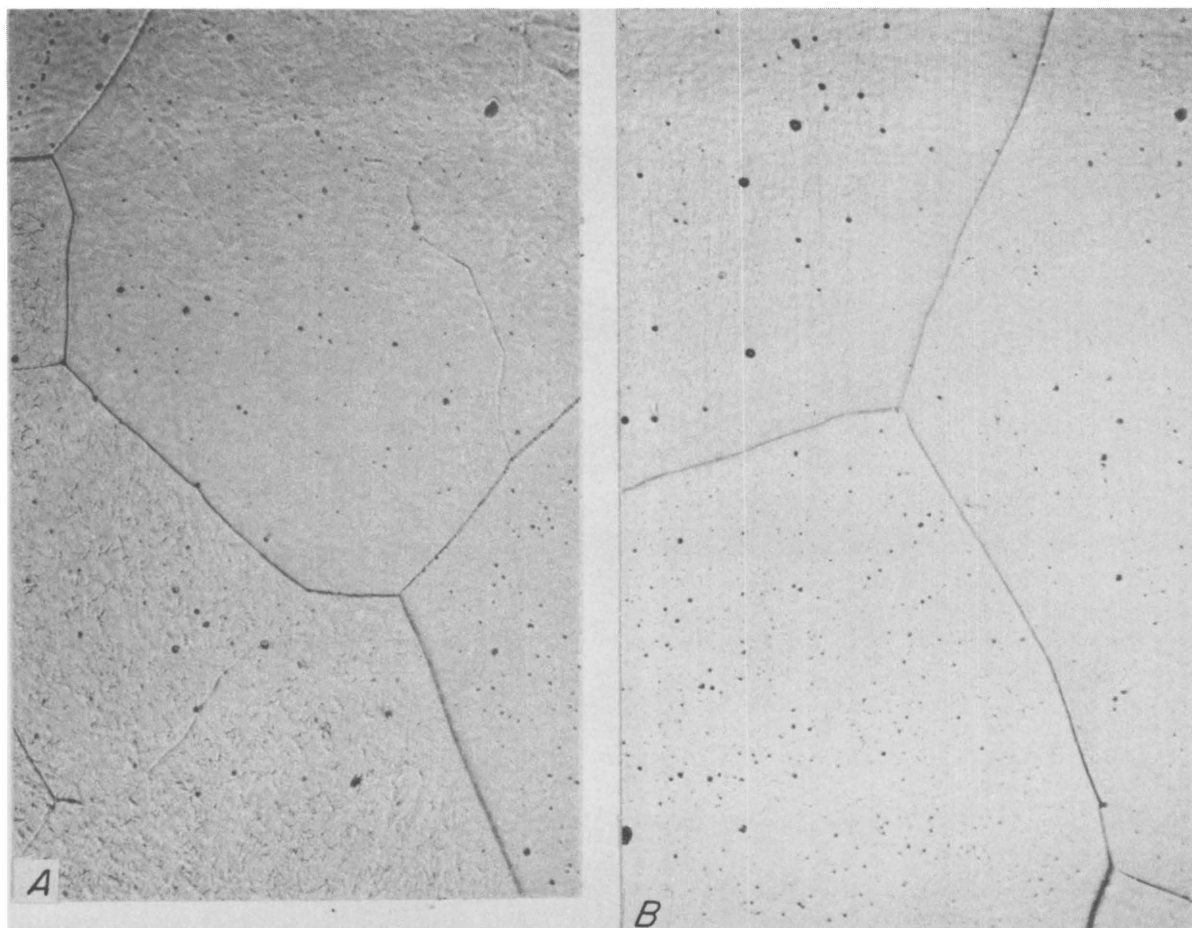


Figure 105.—Photomicrographs of electroslag-melted molybdenum melted with Y_2O_3 flux and deoxidized with carbon (left) and yttrium (right), X 250.

Initial work to break down the as-cast structure was regulated to 50-percent reduction in thickness by metal stops of appropriate thickness. Four billets that failed during early stages of reduction are shown in the top row of figure 106. They represent two ingots that were pressed without deoxidizing additives to the flux, and contained oxygen in excess of 100 ppm. The other ingots in figure 106 were prepared by melting with carbon or yttrium additions to the Y_2O_3 fluxes and were successfully forged with no apparent surface or edge cracking. The oxygen level in these ingots ranged from 49 to 89 ppm. Significant amounts of either yttrium or carbon, or both yttrium and carbon, were also present. This may be an important characteristic, because beneficial effects of controlled amounts of carbon on the fabricability of molybdenum have

been reported (2). The influence of yttria as a dispersed phase may be analogous to that of dispersed thoria in molybdenum (1).

Because of the low working temperature, oxidation of the molybdenum during heating and forging was minimal. Instead of the yellow MoO_3 usually encountered when forging at temperatures above $500^\circ C$, only a thin, tightly adhering blue oxide film was present on the forgings. This was easily removed by vapor blasting.

The structure of the forged specimens was about 50 percent cold worked, and the hardness covered a range of 55 to 63 on the Rockwell A scale. After a recrystallization anneal at $1,600^\circ C$ for 1 hour, the hardness number decreased to Rockwell A-45 to A-49. This is nearly identical to the average as-cast hardness.

The annealed specimens were reformed to a

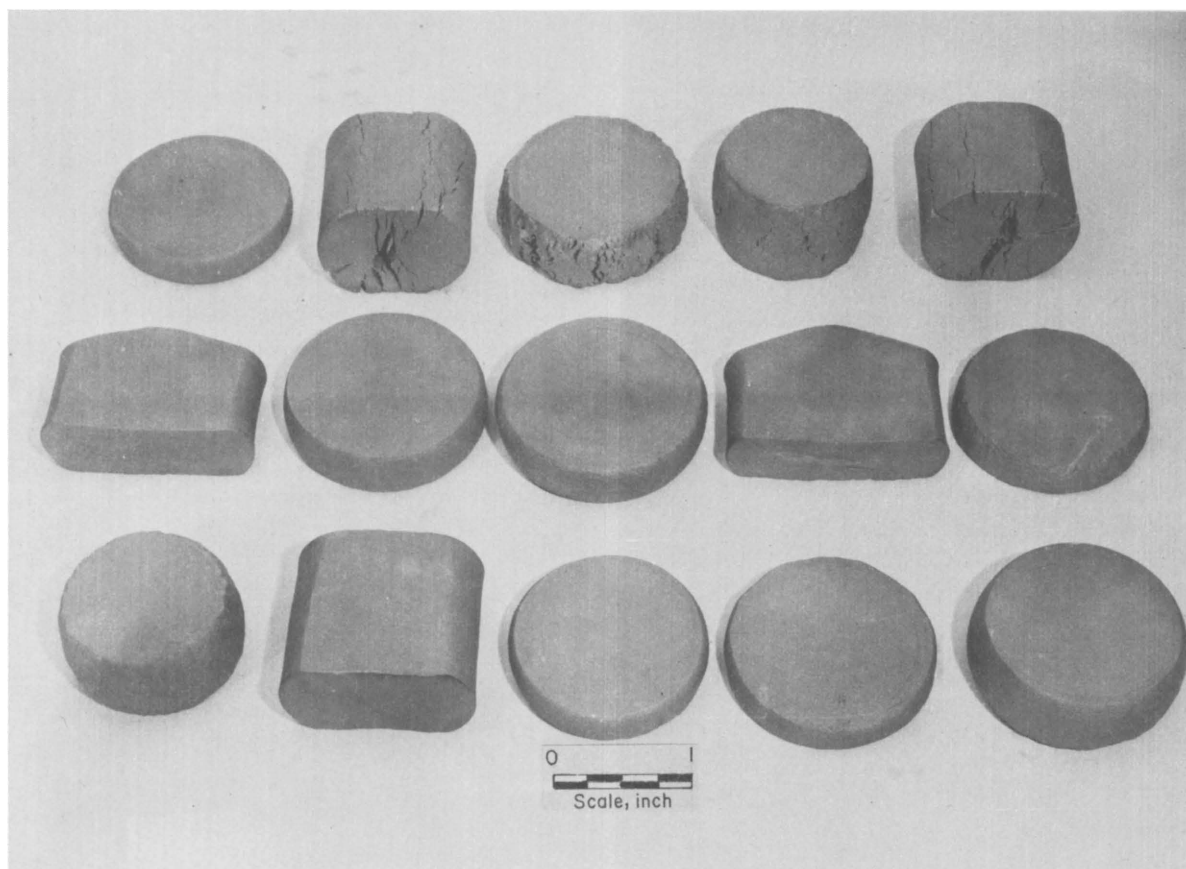


Figure 106.—Primary upset forging of electroslag-cast molybdenum ingots showing effects of deoxidation by flux additives during melting.

nominal thickness of 1.27 cm ($\frac{1}{2}$ -inch) by press forging as described. The majority of the secondary working was done after heating to 500° C; however, to determine the minimum low working temperature possible, some specimens were heated to 400° C and some to 300° C, while others were forged at room temperature. Good results were obtained over the entire temperature range.

To prepare sheet, the press-forged plate was annealed and rolled with no surface conditioning of the plate prior to rolling. Initial reductions of 10 to 50 percent at temperatures ranging from 200° to 500° C were accomplished at a roll speed of 10.67 surface m min⁻¹ (35 surface ft min⁻¹). The lowest temperature at which good results were consistently obtained was 300° C. Best results were obtained by reducing the plate at least 20 percent on the first roll pass. After initial work had been put into the plate, multiple passes could be made through the rolls with no inter-

mediate reheating. This probably was because the sheet temperature was maintained well above the ductile-to-brittle transition temperature by working. On occasion, minor edge and end cracking did occur. An excellent cold-rolled surface finish was obtained by cold rolling to 0.152-cm (0.060-inch) thickness. This represents a nominal 90-percent reduction in thickness from the original 1.27-cm ($\frac{1}{2}$ -inch) annealed plate.

At various stages in the rolling schedule, attempts were made to cross roll in order to change sheet geometry and texture. No satisfactory conditions were determined. All attempts resulted in delamination of the sheet or severe splitting. It appears that this material is extremely sensitive to rolling direction after flow patterns are established.

EVALUATION

The mechanical properties of molybdenum depend upon several factors; included among these

are the amount of work below the recrystallization temperature, the actual working temperature, thermal treatment, strain rate, and metal purity. All of these parameters except metal purity are readily controlled in treatment subsequent to melting. Details of the melting process, however, have not been sufficiently refined to permit control of the impurity level from ingot to ingot; therefore, attempts were made to prepare sheet, from all of the ingots to be tested, by a fixed schedule, and to test under constant conditions in order to evaluate typical properties with metal purity as the only variable.

The primary impurities governing the ductility of arc-melted and powder metallurgy molybdenum are carbon, oxygen, and nitrogen. Of these, oxygen has the most adverse effect on ductility; minute quantities result in severe embrittlement. Nitrogen is also detrimental to ductility but less so than oxygen. The effect of carbon is much less significant than that of either of the foregoing. In addition, the presence of yttrium must be considered, as significant concentrations result from the use of this element to deoxidize the molybdenum during melting and, possibly, from a partial reduction of the yttria flux.

Sheets from seven electroslag and two vacuum-arc ingots were tested to determine comparative tensile properties, hardness, and bend ductile-to-brittle transition temperatures.

The levels of critical impurities in the individual ingots are presented in table 54. These data show significant variations in the amounts of carbon, oxygen, and yttrium that can be related directly to melting practices. As the nitrogen level was very low and varied only slightly, it was considered insignificant for this evaluation. Sheets numbered 575 and 582 in the table were from vacuum-arc-melted ingots. Data for 575 will be used to compare properties of sheet prepared by vacuum-arc and electroslag melting.

All of the sheets to be tested were stress-relieved at 900° C prior to preparation of test specimens to facilitate handling, and again after specimens were prepared, to relieve stresses resulting from slitting and grinding. Some of the specimens were retained in the stress-relieved condition, and the remaining specimens were annealed to effect complete recrystallization. Figure 107 shows a typical photomicrograph of the stress-relieved sheet. A completely cold-worked structure is in evidence. The diamond pyramid hardness num-

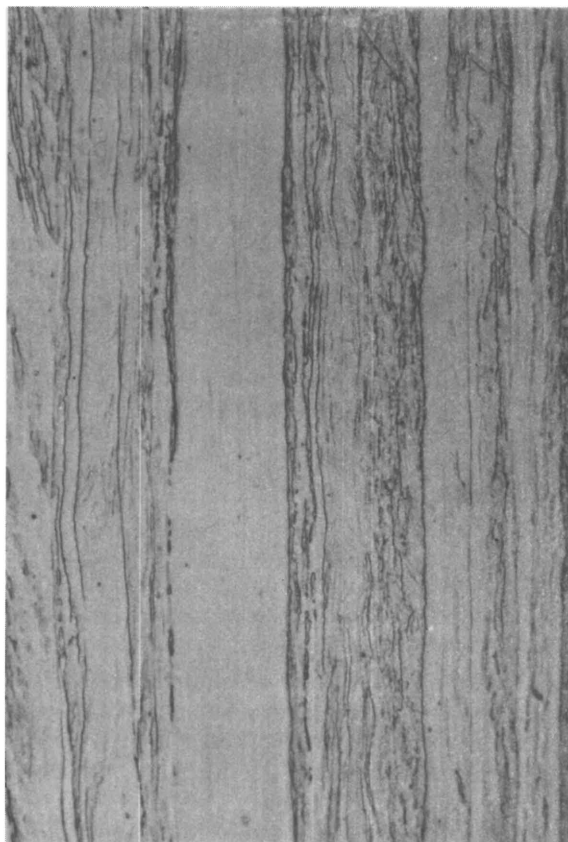


Figure 107.—Sheet from electroslag-melted molybdenum cold worked to ~90-percent reduction and stress-relieved at 800° C, X 500.

ber (DPH) in this condition ranged from 207 to 277.

Despite the large amount of cold work, the recrystallization temperature of the electroslag sheet was quite high. This characteristic is important because recrystallization and strain hardening are the principal mechanisms for altering the mechanical properties of molybdenum. Regardless of composition, complete recrystallization was attained by heating to $1,400^{\circ} \pm 50^{\circ}$ C for 1 hour. Typically, the recrystallization temperature of unalloyed commercial molybdenum follows a curve similar to the one shown in figure 108. This would make the recrystallization temperature for electroslag sheet, cold-worked to approximately 90-percent reduction, equivalent to that for unalloyed arc-cast sheet reduced by rolling almost 30 percent. This means that the elevated temperature strength, up to 1,400° C, of the electroslag sheet should be superior to that of typical arc-cast

Table 54.—Major impurities in molybdenum test sheet

Sheet No.	Melting mode ¹	Impurities, ppm				
		C	O	H	N	Y ²
502	ES	11	49	1.6	6	<300
503	ES	31	47	<1	6	480
506	ES	116	70	1.5	5	340
510	ES	19	89	1.2	7	640
511	ES	21	81	1.7	7	550
513	ES	16	65	1.4	6	740
575	VAM	16	35	<1	5	<300
582	VAM	19	44	<1	<5	<300
587	ES	19	98	2	<5	<300

¹ ES—Electroslag ingot; VAM—Vacuum-arc-melted ingot.² 300 is lower detection limit for yttrium with the method of analysis employed.

unalloyed sheet at the same temperature. A single-phase structure, free of precipitates, was typical of all the sheet examined. An example of this sheet is shown in figure 109. The grain size ranged from ASTM 5 to 8, and the hardness from DPH 177 to 196.

Recrystallization of the vacuum-arc-cast material was achieved by heating to 1,100° C for 1 hour. The microstructure is shown in figure 110. It cannot be distinguished from that of the electroslag sheet already shown. The grain size of this material ranged from ASTM 5 to 7. The hardness ranged from DPH 181 to 187.

As the impurities carbon, oxygen and yttrium varied over a wide range from ingot to ingot, and no satisfactory means were found to closely control the concentration of any of these elements, selection of a typical ingot to compare with the vacuum-arc cast material was not possible. Therefore, to obtain a representative evaluation, it was necessary to examine sheet from three individual electroslag ingots. These ingots contained the maximum amount of one of the major impurities and relatively low levels of the other two. The influence of the various elements on hardness is shown in figure 111. This chart

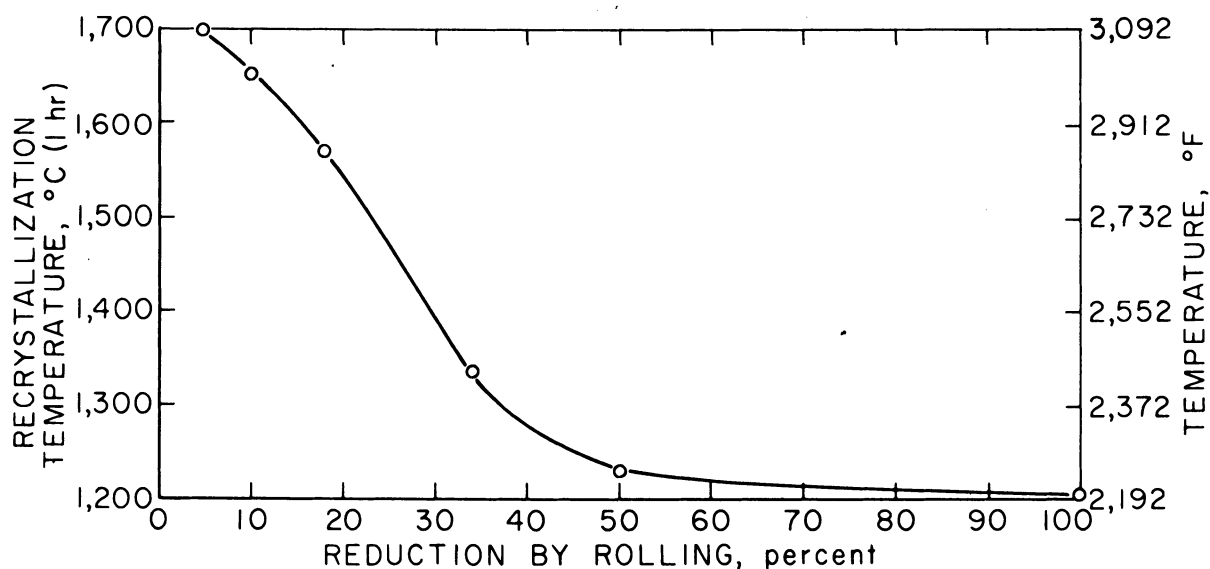


Figure 108.—Recrystallization curve for commercial (unalloyed) molybdenum sheet.

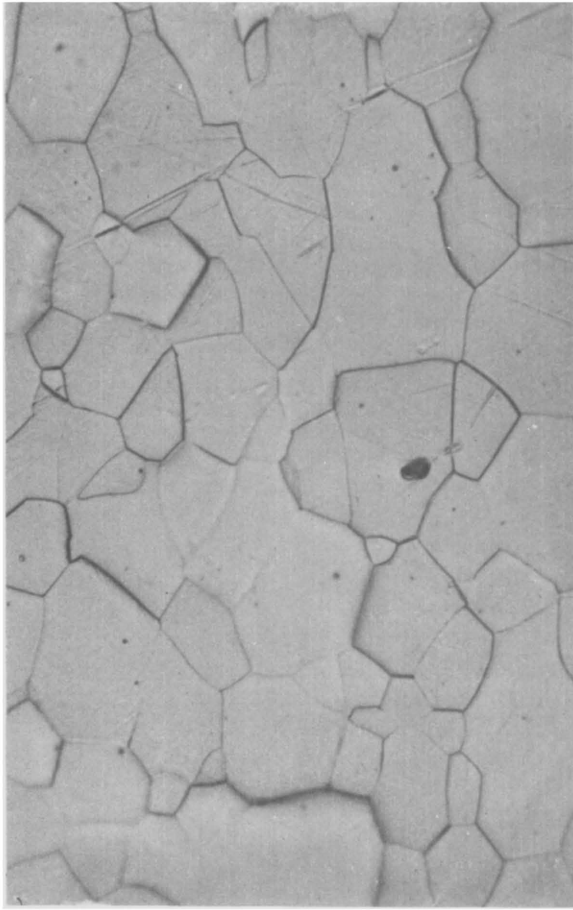


Figure 109.—Sheet from electroslag-melted molybdenum cold worked to ~ 90 -percent reduction and recrystallized at $1,400^{\circ}\text{C}$ for 1 hour, X 500.

shows that the recrystallized hardnesses for the arc-melted sheet and all of the electroslag sheet are nearly equal. The fact that stress-relieved sheet from the high-oxygen (100 ppm) and high-yttrium (740 ppm) ingots is harder than as-worked (cold-rolled) sheets from these ingots indicates the occurrence of age or precipitation hardening in these two sheet products. Examination of the hardness data from all electroslag molybdenum sheet tested indicates a linear increase in room temperature hardness of sheet as a function of both carbon and yttrium levels. A plot of hardness against oxygen level failed to reveal any definite trends.

Bend Ductility

Molybdenum, like other body-centered cubic

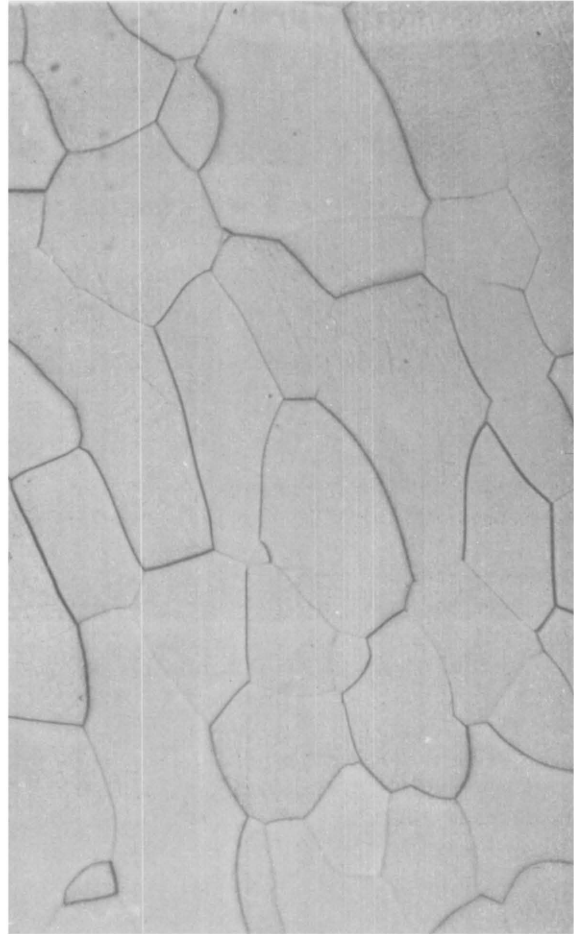


Figure 110.—Sheet from vacuum-arc-cast molybdenum cold worked to ~ 90 -percent reduction and recrystallized at $1,100^{\circ}\text{C}$ for 1 hour, X500.

metals, exhibits a ductile-to-brittle transition as the temperature is decreased. This temperature range depends upon several factors, including the specimen geometry, surface preparation, and method and rate of stress application.

In the bend tests performed, all factors listed above were maintained constant in order to arrive at a representative comparison of properties. The test specimens were prepared from 0.152-cm (60-mil) sheet, the edges of which were ground to a flaw-free finish of 32 RMS or better. The longitudinal direction of the test blank was oriented parallel with the rolling direction of the sheet.

The bend transition temperature from ductile to brittle behavior was judged to be the lowest

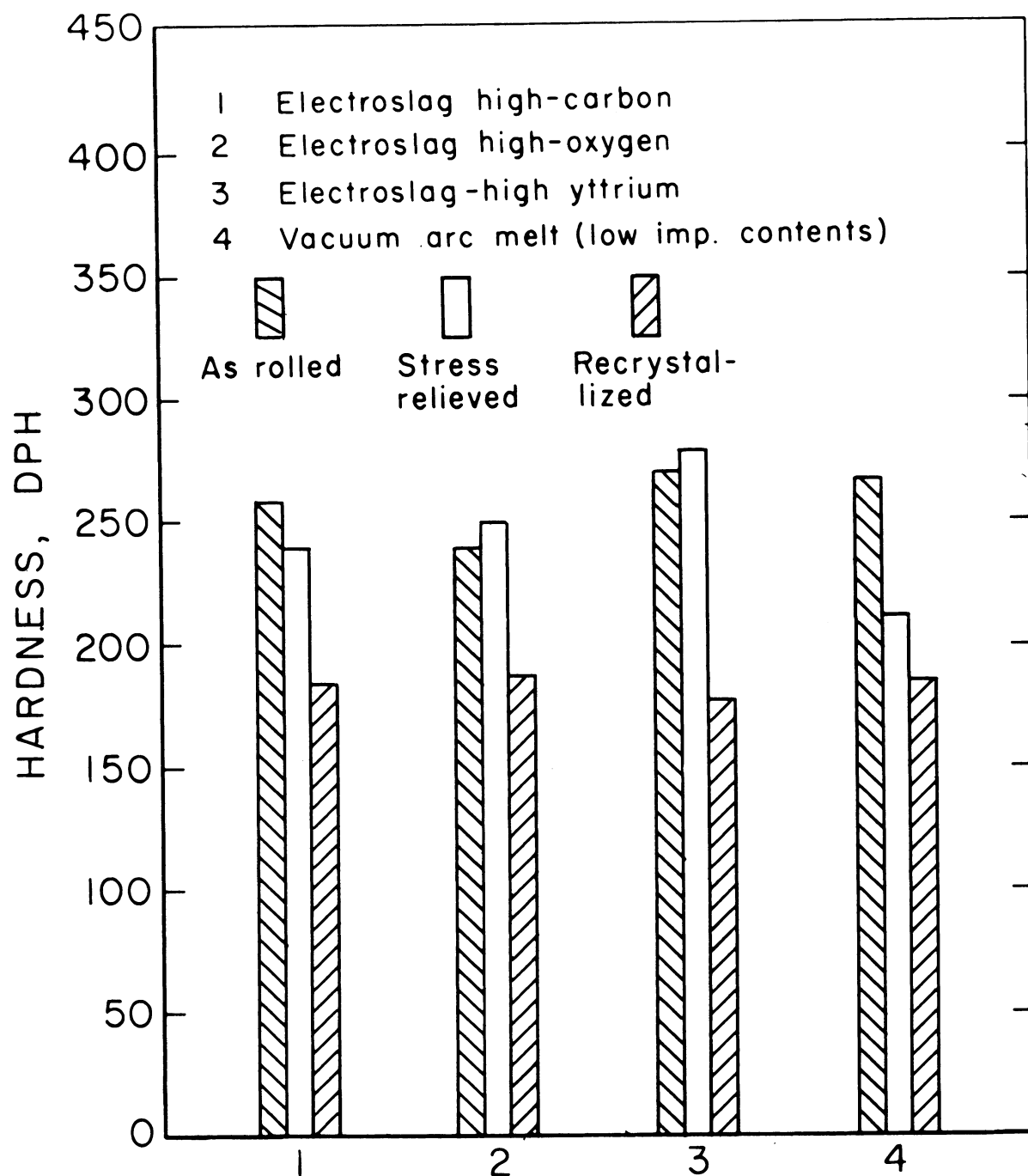


Figure 111.—DPH hardness of 0.152-cm (0.060-inch) sheet rolled from electroslag- and arc-melted molybdenum ingots.

temperature at which a sound 90° bend could be produced; a maximum spring back of 5° was allowable.

A comparison of the ductile-to-brittle transition temperature (DBTT) of electroslag- and arc-

melted sheet is shown in figure 112. These data indicate that stress-relieved sheet prepared from electroslag-melted molybdenum ingots should be more readily fabricated by bending than that from arc-melted ingots. All of the electroslag

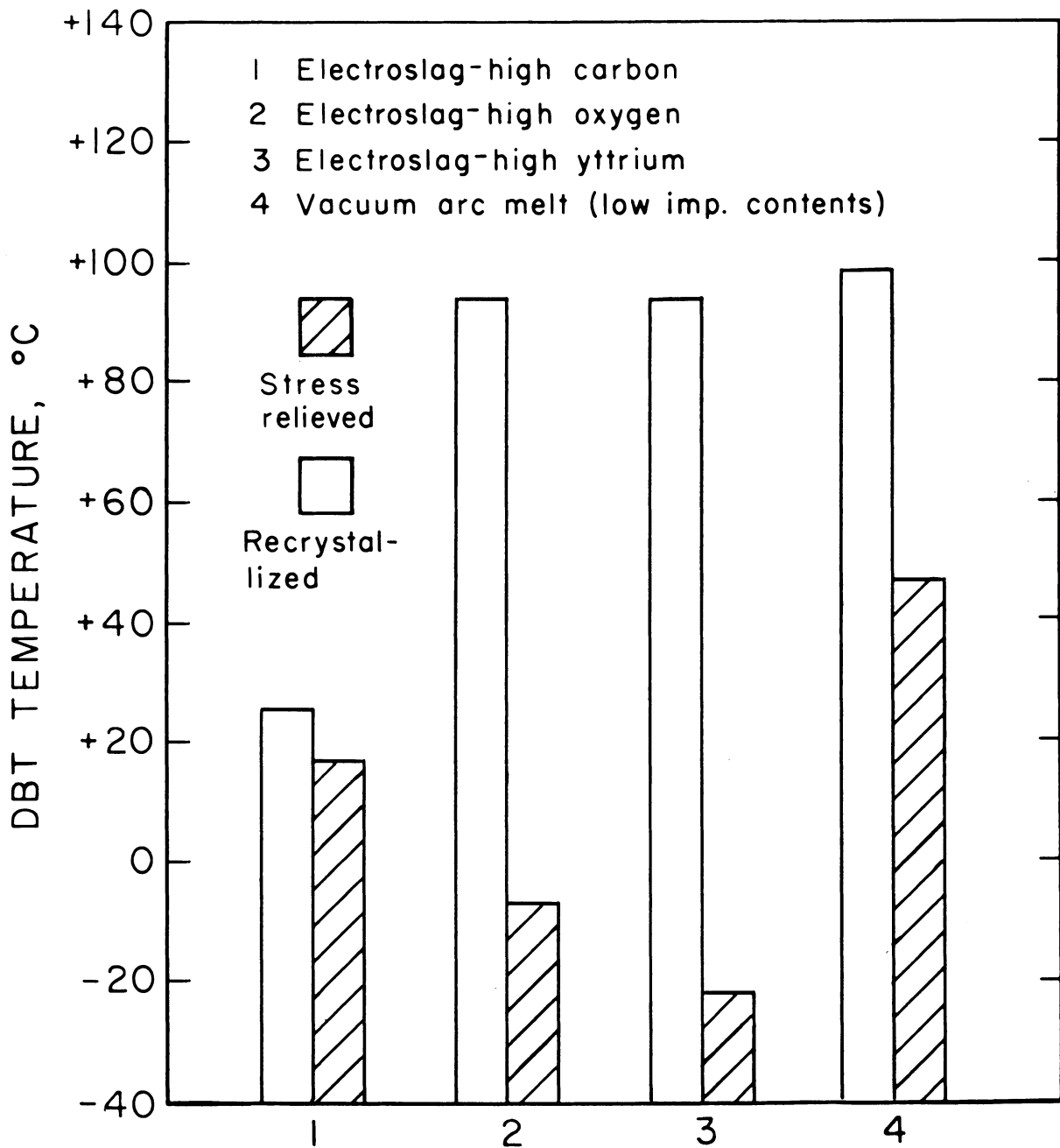


Figure 112.—Ductile-to-brittle transition temperatures of 0.152-cm (0.060-inch) sheet rolled from electroslag- and arc-melted molybdenum ingots.

sheet tested displayed a DBTT in the stress-relieved condition below room temperature. Both stress-relieved and recrystallized sheets from ingots containing high carbon transformed from ductile to brittle behavior below room temperature, and therefore should be suitable for room

temperature fabrication. On the other hand, the DBTT of the arc-cast sheet was well above room temperature for both conditions. These data indicate that severe deformation without heating is precluded for this material. Recrystallized electroslag sheets with high oxygen and high yttrium

contents have transition temperatures comparable with that of the recrystallized arc-cast sheet.

Figure 113 shows a plot of bend-angle versus

temperature for the molybdenum sheet under discussion. These data indicate the relative amounts of deformation which can be success-

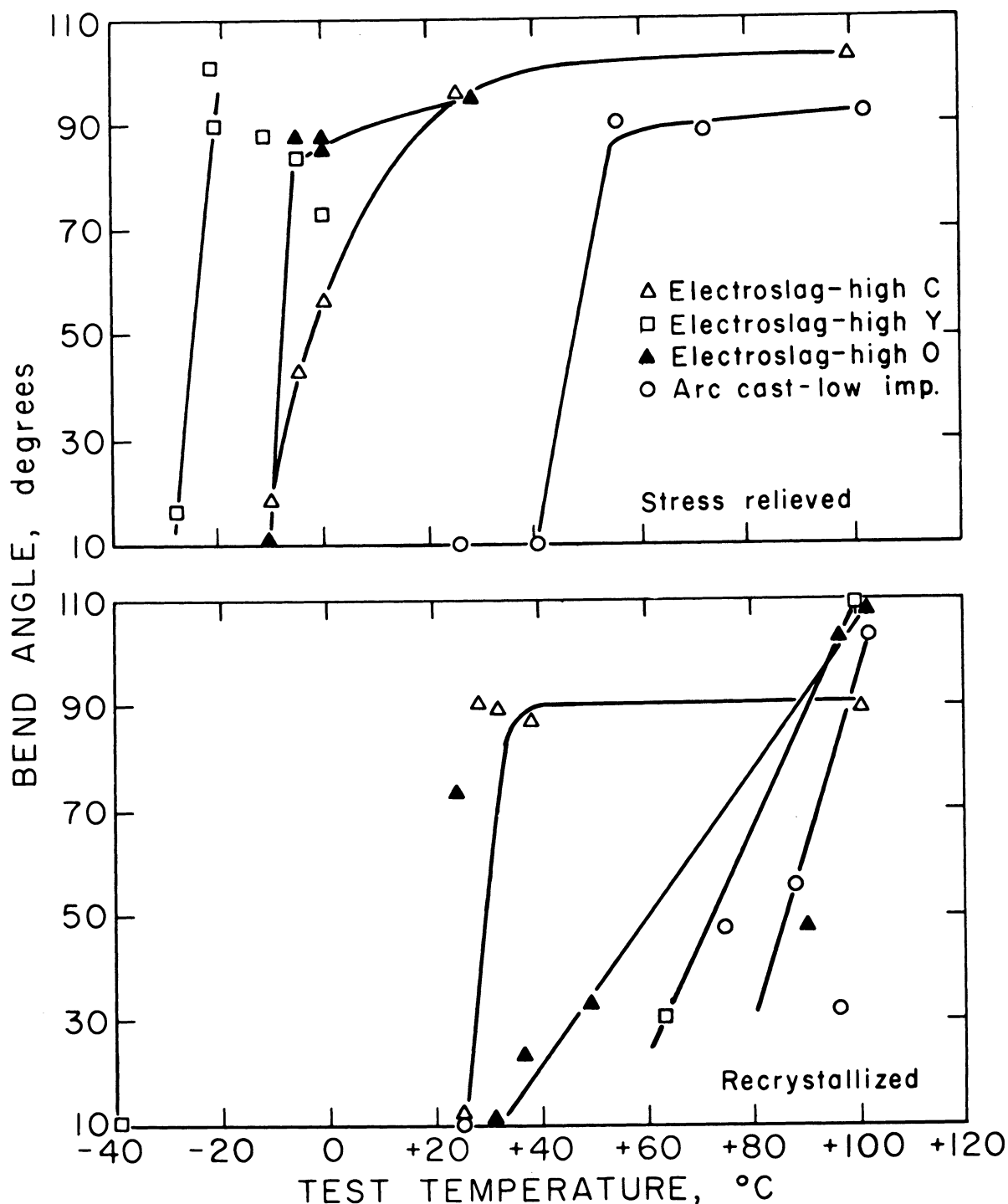


Figure 113.—Bend angle versus temperature showing ductility of 0.152-cm (0.060-inch) sheet from electroslag and arc-cast molybdenum ingots.

fully performed at various temperatures. The superior fabricability of the electrosag sheet is again indicated.

It is fairly obvious from the spread in data that rather large variations in the bend transition temperature can result from ingot chemistry and, very possibly, from the size and distribution of excess phases. It is believed that finely dispersed phases are present, particularly in strained structures, but cannot be seen under normal magnification. Undoubtedly, surface condition, which was as-rolled and therefore variable, exerted a considerable amount of influence on the tests. The effects of processing should be relatively small because efforts were made to control the thermal and mechanical history of the sheet.

Tensile Properties

Tensile tests were performed on sheet from the three electrosag ingots and one vacuum-arc-melted ingot. The structural conditions evaluated were stress-relieved and recrystallized. Tests were conducted at room temperature, 200°, 600°, 1,000°, 1,400°, 1,600°, and 2,000° C. Test coupons were prepared with the longitudinal direction of the blanks parallel to the rolling direction of the sheet.

The room temperature tests were conducted on a Baldwin Universal Test Machine utilizing a calibrated P₅₃M 2.54-cm (1-inch) extensometer to measure strain. All elevated-temperature tests were conducted on a Marquardt TM-1 test machine. It was equipped for self-resistance heating within a controlled environment chamber. A class B non-averaging extensometer was used with this machine; consequently, strain measurements were not sufficiently accurate to determine the modulus at elevated temperatures. Both room temperature and elevated temperature tests were conducted with a uniform strain rate of 0.05 cm/cm/min until failure of the specimen occurred.

A summary of the tensile properties of 0.152-cm (60-mil) sheet rolled from electrosag and as-cast molybdenum ingots is presented in table 55. These data show that the tensile strength of stress-relieved sheet from room temperature through 600° C varies little with change in the level of oxygen, carbon, or yttrium. At these temperatures, sheet from all of the electrosag ingots has a higher tensile strength by 18,000 to 20,000 psi than does sheet from the arc-cast molybdenum ingots. It should be noted here that the arc-cast material, which has a room tempera-

ture tensile strength of greater than 100,000 psi, compares reasonably well in strength with commercial, unalloyed, arc-cast molybdenum sheet. At 1,000° C pronounced differences in the pattern are seen. These changes are more clearly seen by examination of figure 114, which shows graphically a rapid decline in the tensile strength of sheet from electrosag ingots that contain relatively high levels of yttrium. The tensile strength of the high-oxygen, stress-relieved electrosag sheet is significantly higher at this temperature than that of the other three compositions. It is noteworthy that it also compares more favorably at this temperature with the tensile strength of the arc-cast sheet material. At 1,400° C the sheet with the high oxygen content is twice as strong as the arc-cast or the remaining two electrosag materials. Tensile strength declined gradually from the 1,400° C tests through test at 2,000° C, and became nearly equal for all of the tests at the higher temperatures.

The yield strength at 0.2 percent offset of all materials tested tends to follow the trend established for tensile strength properties up to and including the 600° C tests. This is illustrated in figure 115. At 1,000° C, however, the yield strengths of stress-relieved, arc-cast sheet and high-carbon electrosag sheet are nearly equal at 45,000 and 47,000 psi, respectively. They exceed the yield strength of the other two materials in this condition by 10,000 to 19,000 psi.

Any meaningful correlation between strength and elongation for any of the materials tested was impossible to attain. The data displayed a considerable amount of scatter, as can be observed by examination of table 55. This is undoubtedly a result of surface affected zones on the test coupons and might have been avoided by grinding or chemical milling of the specimens.

Creep Rupture

Data for creep rupture tests performed are shown in table 56. These data, when plotted, indicate that the 100-hour stress rupture strength of this material is about 46,000 psi at 900° C. This is much higher than published values which show the 100-hour rupture strength to average around 30,000 psi for commercially pure unalloyed molybdenum.

CONCLUSIONS

The potential of electrosag melting for preparing high-yield molybdenum ingots has been demonstrated. Three important factors influence the low processing losses experienced during

Table 55.—*Tensile properties of 0.152-cm (0.060-inch) sheet rolled from selected electroslog and vacuum-arc-cast molybdenum ingots*

Sheet number	Type of sheet	Major impurity	Condition ¹	Test temperature °C	Tensile strength, 1,000 psi	Yield strength 0.2 pct offset, 1,000 psi	Elongation, percent
506	Electroslog	Carbon	SR	Room	120	111	45
			SR	200	95	87	44
			SR	600	86	76	40
			SR	1,000	54	47	56
			SR	1,400	7	6	75
			Rec	Room	76	52	38
			Rec	200	48	14	65
			Rec	600	36	11	68
			Rec	1,000	24	10.5	74
			Rec	1,400	7	6	78
			Rec	1,600	8	6	73
			Rec	2,000	3	2	49
513	 do	Yttrium	SR	Room	123	108	37
			SR	200	98	86	42
			SR	600	86	76	29
			SR	1,000	36	28.5	60
			SR	1,400	7	6	68
			Rec	Room	34	(²)	(²)
			Rec	200	43	9.5	70
			Rec	600	27	8	62
			Rec	1,000	14	6.5	60
			Rec	1,400	8	6	42
			Rec	1,600	8	5.5	45
			Rec	2,000	3	3.5	26
587	 do	Oxygen	SR	Room	123	102	26
			SR	200	96	85.5	42
			SR	600	85	75	39
			SR	1,000	62.5	54	38
			SR	1,400	14	14	64
			Rec	Room	44	41	2
			Rec	200	44	12	65
			Rec	600	39.5	8.5	62
			Rec	1,000	23.5	7	57
			Rec	1,400	9.5	6	36
			Rec	1,600	9.5	5	37
			Rec	2,000	5	3	39
575	Vacuum-arc melted	None	SR	Room	102	96	49
			SR	200	76.5	65.0	14
			SR	600	65	59	9
			SR	1,000	50	45	11
			SR	1,400	7	6	14
			Rec	Room	55	43	(³)
			Rec	200	44	12	(³)
			Rec	600	32	10	(³)
			Rec	1,000	17	8	(³)
			Rec	1,400	8	6	(³)
			Rec	1,600	7	6	(³)
			Rec	2,000	3	3	(³)

¹ SR = stress relieved; Rec = recrystallized.² Specimen was brittle.³ Specimen was brittle and broke outside the gage marks.

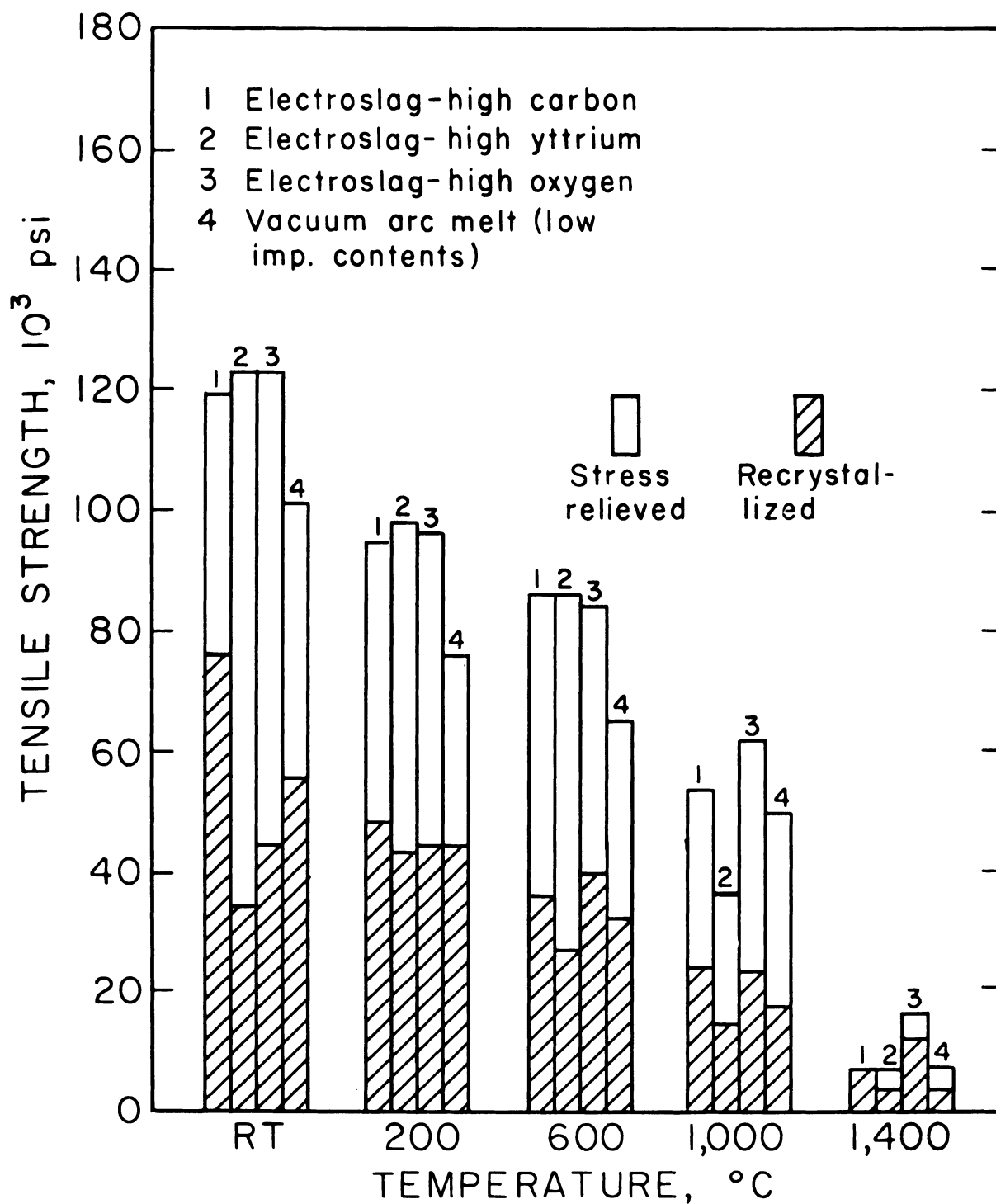


Figure 114.—Tensile strength of 0.152-cm (0.060-inch) sheet rolled from electroslag and arc-melted molybdenum ingots.

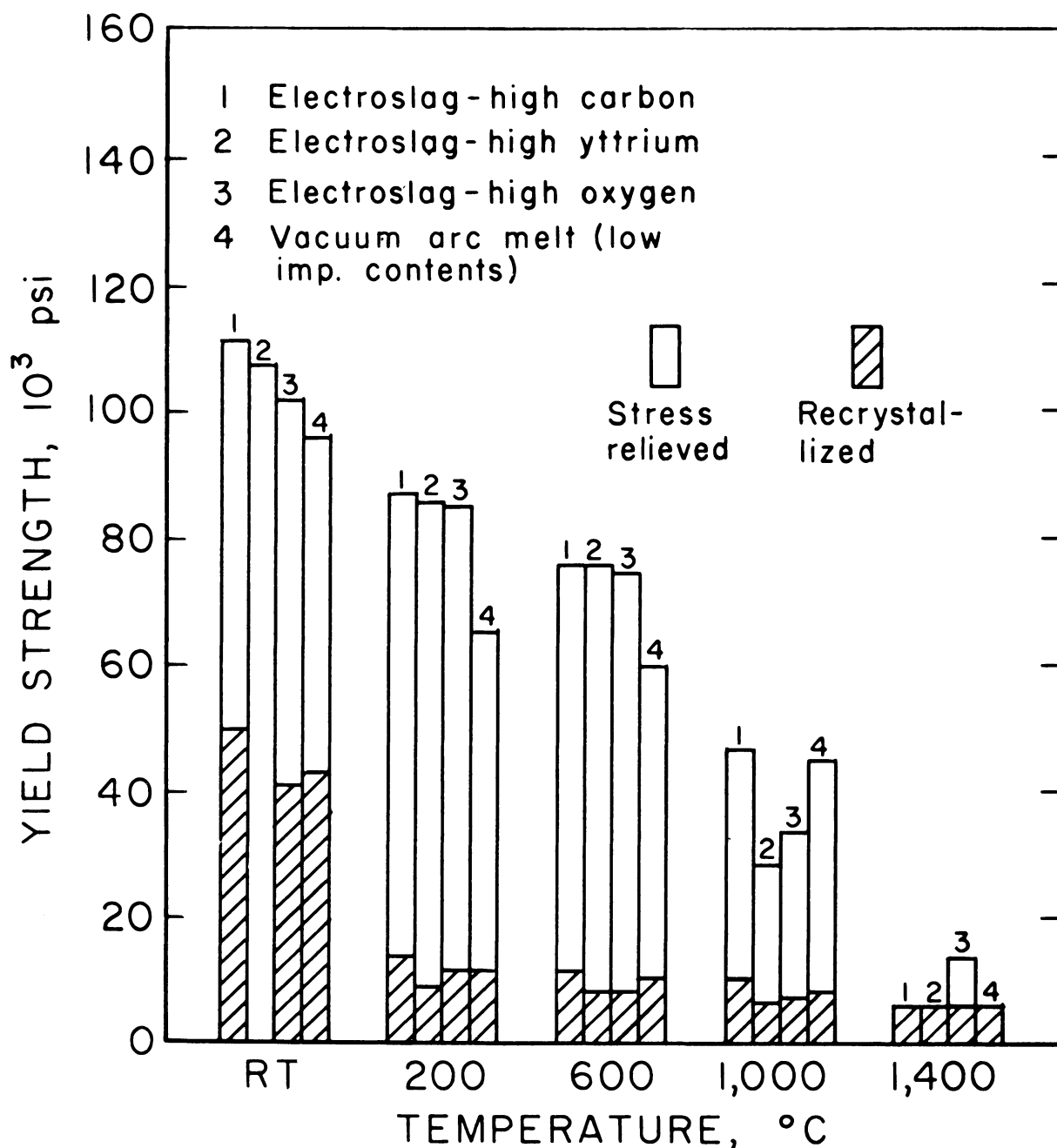


Figure 115.—Yield Strength at 0.2-percent offset of 0.152-cm (0.060-inch) sheet rolled from electroslag- and arc-melted molybdenum ingots.

metal working experiments. These are (1) excellent ingot surface conditions, which practically preclude the necessity for sidewall conditioning, (2) absence of shrinkage cavity and ingot collar so that cropping of ingot top is not required, and (3) minimum loss of metal through oxidation of ingot during fabrication because of the ability of

electroslag-melted ingots to be forged by conventional techniques at low temperatures below the oxidation temperature of molybdenum.

Techniques were not developed to precisely control the level of critical impurities. It appears that higher impurity contents are more tolerable in the electroslag ingots than in arc-cast ingots,

Table 56.—Stress-rupture testing of electroslag molybdenum sheets
[specimen 513, stress-relieved condition]

Temp, °C	Stress, psi	Test life, hours	Elonga- tion, pct	Reduc- tion of area, pct
900	75,000	0	2	—
900	60,000	1.9	8	66
900	50,000	28.2	11	66
900	38,000	>200	¹ 2	¹ 2
1,200	10,000	>112	(¹)	(¹)
1,200	20,000	.1	33	73
1,200	30,000	.7	14	49

¹ Test incomplete; specimen did not fail in this time.

possibly because of the nature of their occurrence and the method in which they are distributed. In the instance of oxygen in arc-cast molybdenum products, loss of ductility and mechanical strength normally results at levels far below those seen in this work.

The mechanical properties of sheet products

from electroslag ingots appear to be generally superior to those of arc-cast ingots. However, arc-cast ingots containing similar impurities were not evaluated; therefore, it cannot be said positively that the improved mechanical properties are due to melting practice rather than composition.

A separate investigation of the effects of finely dispersed oxide phases indicates that precipitates so small as to require electron microscopy for their detection have definite effects upon the mechanical properties of heavily worked, powder metallurgy molybdenum and tungsten. We surmise that the electroslag melting process might be a novel method for introducing fine and uniformly dispersed phases in fused molybdenum without the requirement for heavy work to produce similar results. This might have influenced the successful primary fabrication by upset forging, at such relatively low temperatures.

On the basis of an extensive literature search, no further reports have been found that deal with the electroslag melting of molybdenum or other refractory metals.

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CHAPTER 16.—OTHER SLAG-MELTING PROCESS AND VARIATIONS OF THE ELECTROSLAG PROCESS¹

By P. G. Clites,² R. A. Beall,³ and R. H. Nafziger

Although the electroslag process offers a number of advantages over conventional secondary melting techniques, shortcomings of the process exist. Included among the disadvantages are (1) the requirement for a consumable electrode which must be briquetted, cast, or forged, and which contributes to the overall cost, (2) size limitations for thin slabs and ingot lengths, and (3) the possibility of poor ingot bottoms and the necessity for melting the flux in the crucible in the case of solid flux starting. In addition, electroslag melting is considered to be less efficient and to have higher energy consumption than vacuum-arc melting (21). In recent years, several modifications to the conventional electroslag process as described in the introduction have been proposed. In addition, a number of completely new but related flux melting processes have been studied. These wholly or partially circumvent the aforementioned disadvantages of the electroslag process. The objective of this chapter is to describe these variations and enumerate their advantages.

THE INDUCTOSLAG MELTING PROCESS

Inductoslag melting is an induction melting process in which the metal is melted in a split, water-cooled copper crucible. The crucible has one or more longitudinal slits (usually four to six) which prevent attenuation of the field of the surrounding work coil. A cover of molten flux is maintained in the crucible, and the ingot is electrically insulated from the walls of the copper crucible by a thin layer of solid flux which forms on the crucible walls during the melting process. This insulating layer of flux prevents the molten

metal from shorting out the segments of the crucible, a problem encountered by other investigators who attempted to use a split metal crucible (20).

The principal advantage of this melting technique is the capability of melting loose material. This makes it unnecessary to fabricate a consumable electrode as in vacuum-arc melting and electroslag melting. Two recent developments in the field of nonconsumable-electrode-arc melting, Westinghouse's "Durarc" (1) and Schlienger's "Rotatrod" (12), offer a similar advantage. Elimination of the need for fabricating a consumable electrode is particularly advantageous for reclaiming titanium scrap. Electron beam melting systems are also being considered for titanium scrap melting (18).

Inductoslag melting is, therefore, one of several schemes proposed in recent years for melting titanium in which a consumable electrode need not be fabricated. Interest in such schemes has come about owing to concern for a growing titanium scrap problem, either real or imagined (6), and as a means of reducing the cost of titanium through better utilization of available scrap.

Equipment

The initial tests to determine the feasibility of the inductoslag melting process were conducted in a small furnace powered by a 75-kw, 10-kHz motor generator. Ingots produced in this furnace were limited to an 8.9-cm (3½-inch) diameter by the power supply available and to approximately a 30-cm (11.8-inch) length by the physical dimensions of the furnace. To further evaluate the process by preparing larger ingots, a second furnace was built which was capable of producing ingots of greater diameter and greater length. A 100-kw, 10-kHz power supply was available for this work and proved to be adequate for producing ingots 12.7 cm (5 inches) in diameter. The furnace was designed to accom-

¹ Adapted in part from Bureau of Mines Report of Investigations 7268, 1969; Trans. Vac. Met. Conf., 1969, pp. 431-449; Light Metals 1972, pp. 325-351 (1972).

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moderate ingots 100 cm (39 inches) long, a length considered adequate for the work proposed.

The melting crucible was the only unconventional component of this furnace, and it did not differ in its basic design from split crucibles described by others (16–17) for induction melting. A typical crucible of the type used is shown in figure 116. Figure 117 is a longitudinal section of this crucible and shows the relative position of the work coil, the ingot, and the flux cover during melting. Each of the four segments of this crucible had internal water cooling, and each segment was bolted to the lower, nonsegmented portion of the crucible, which served as a water manifold. Water inlet and outlet connections for the segments were through O-ring-sealed passages in the flanges. Each of the four segments was electrically insulated from the other segments and from the lower section of the crucible. Alumina rods, 0.64 cm ($\frac{1}{4}$ inch) in diameter, served as spacers along the length of the slits and also sealed the slits to prevent molten flux from leaking out of the crucible during melting.

Figure 118 shows an alternate crucible design in which the crucible was slit only in the melting zone. Both crucible designs were satisfactory, and, if the partially segmented crucible shown in figure 118 was less efficient than the fully segmented design, the difference was too small to be detected in the experiments conducted thus far. Crucibles of the partially segmented design and with a rectangular cross section have also been effectively used to produce ingots with a 6.3-cm ($2\frac{1}{2}$ -inch) by 10-cm (4-inch) rectangular cross section.

The crucible was installed in a vacuum chamber with provisions for sidefeeding loose material into the open top of the crucible and for withdrawing the resultant ingot downward as it was formed. The main chamber was a horizontal cylindrical tank approximately 75 cm ($29\frac{1}{2}$ inches) in diameter and 100 cm (39 inches) long. The material for melting was placed in a hopper above the furnace and was side-fed into the crucible by means of a vibrating feeder. The melting operation was observed through two view ports, one directly above the crucible in the top of the furnace and one in the furnace door.

Ingot withdrawal was by means of a motor-driven screw drive which was manually controlled by the furnace operator. As material was added to the crucible, the ingot was withdrawn to maintain the top of the ingot at a more or less constant level in the crucible. The ingot was

withdrawn through the bottom of the crucible into a 20-cm (8-inch) diameter extension tube, which provided sufficient length to accommodate an ingot 100 cm (39 inches) long.

Figure 119 shows the crucible and work coil installed in the furnace chamber. The work coil for this particular installation was a nine-turn coil of 1.27-cm ($\frac{1}{2}$ -inch) diameter, heavy-walled copper tubing. Power to the work coil was carried through the chamber wall with a coaxial lead-through, visible in figure 119 at the left of the crucible. The power supply was a 100-kw, 10-kHz motor-generator.

Melting Procedure

Melting was initiated by placing a starting stub and an initial charge of metal and flux in the crucible with the initial charge of metal centered in the work coil as shown in figure 120. The starting stub was a short length of the metal to be melted that had been machined to conform to the inside diameter of the crucible. This stub was fastened to the withdrawal rod at the bottom of the furnace as shown in figure 120. Suggested dimensions of starting stubs for various ingot diameters are given in table 57. A shoulder at the bottom of the starting stub prevented molten flux from leaking out the bottom of the crucible at the beginning of the run.

Table 57 also includes weights of the initial charge of metal and flux placed in the crucible to initiate each melt. Ideally, the initial charge of metal was a short cylinder with a diameter sufficiently less than the diameter of the crucible to provide an annular space between the initial charge of the metal and the crucible wall. The initial charge of granular flux was placed in this annular space to provide a supply of flux between the metal and the crucible sidewall when melting started. Calcium fluoride was the only flux used for inductoslag melting titanium. Choice of flux materials and flux treatment was based on experience gained during electros slag melting of titanium as described in chapter 7.

Many variations to the starting procedure were possible, but the procedures outlined above made starting easiest. Satisfactory results were obtained, for instance, when the initial charge of metal consisted of irregularly shaped pieces of scrap with which the initial charge of flux was interspersed. It was also satisfactory to reduce the diameter of the upper 2 to 5 cm (0.8 to 2 inches) of a slightly longer starting stub and let this serve as the initial charge of metal.

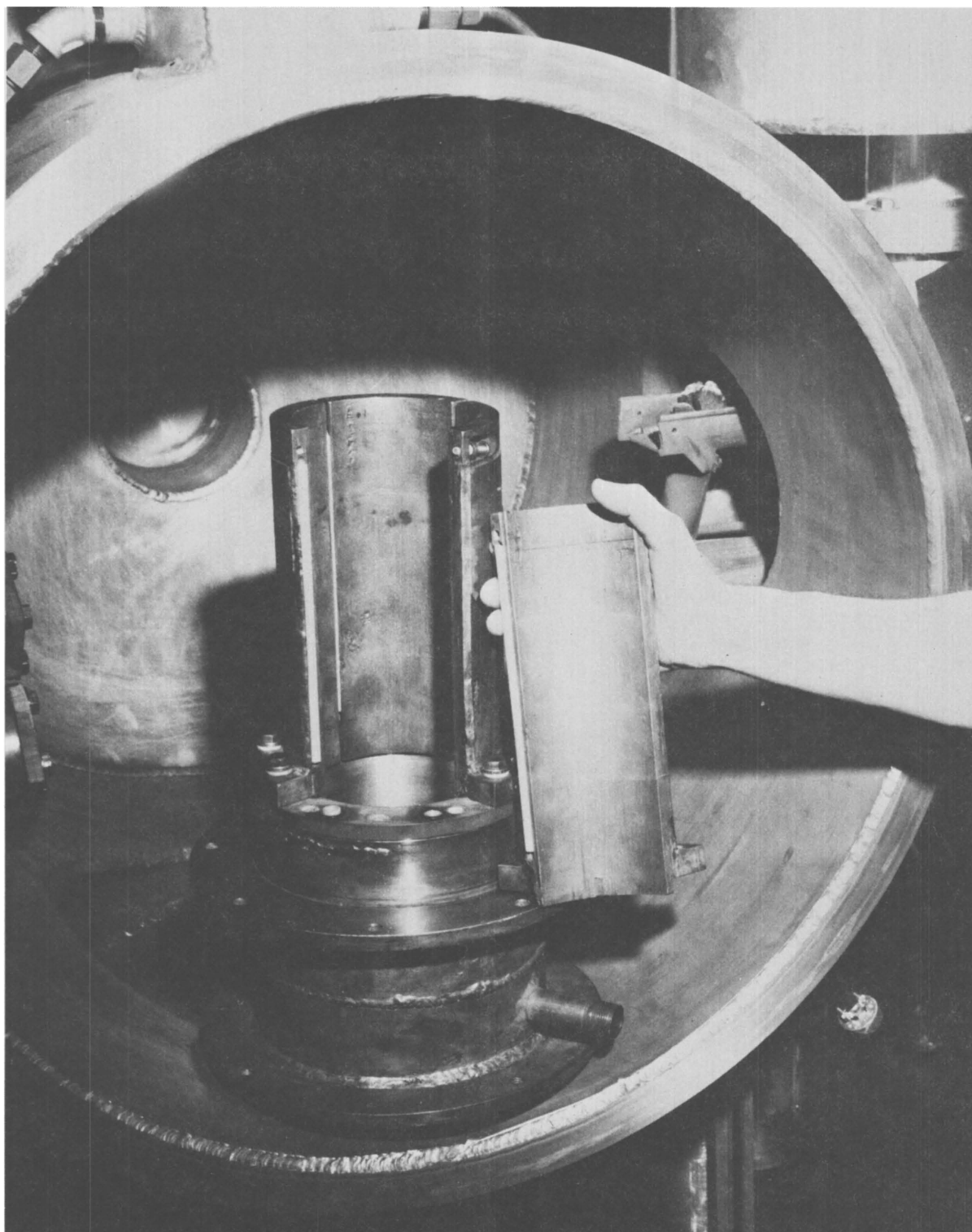


Figure 116.—Segmented, 12.7-cm (5-inch) diameter, water-cooled copper crucible and water manifold.

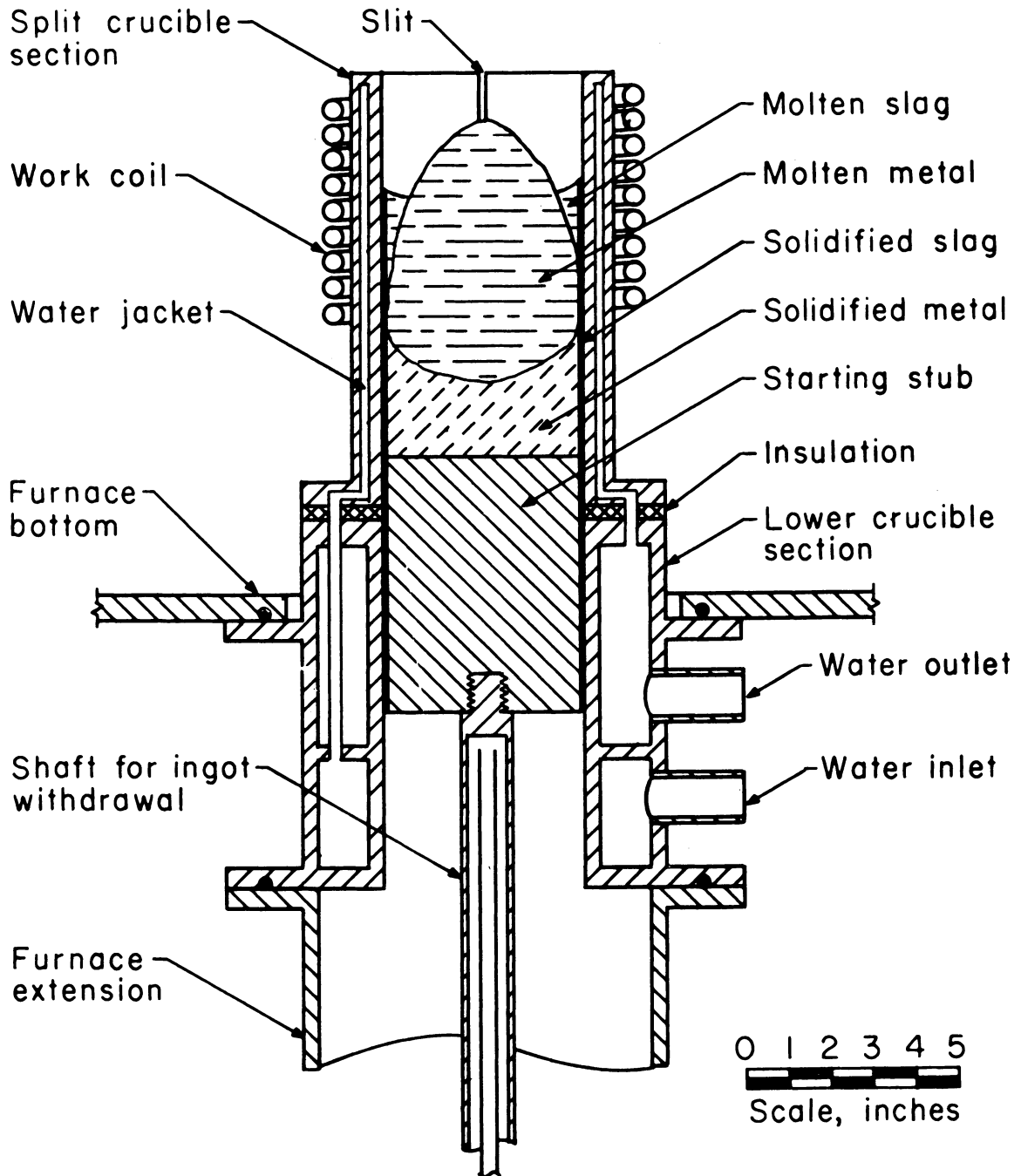


Figure 117.—Longitudinal section of crucible with ingot in melting position.

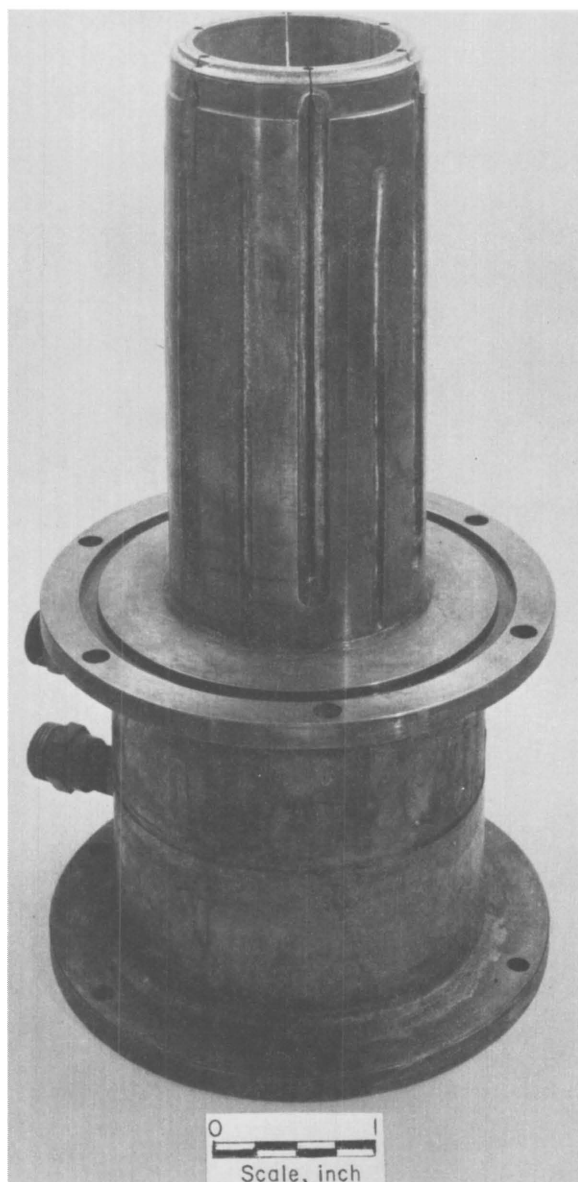


Figure 118.—Partially segmented 8.9-cm ($3\frac{1}{2}$ -inch) diameter, water-cooled, copper crucible.

The material to be melted was loaded into the sidefeeding tank along with granular flux. It was convenient to mix the flux with the metal and feed both flux and metal simultane-

ously when melting turnings, chopped plate, or sponge metal. The metal and flux mixture was gravity-fed onto a vibrating feeder, which carried the material to the crucible. With previously melted material, such as turnings and chopped plate, approximately 4 weight-percent of calcium fluoride was required. This flux, when added with the metal being melted, replenished the flux pool, which was constantly being depleted by the layer of flux which formed along the crucible wall and was withdrawn with the ingot. With sponge metal, 6 to 8 weight-percent of flux was required. More flux was needed for sponge melting because the ingot wall was rougher than when previously melted material was used. In general, increased volatiles in the feed stock resulted in increased roughness of the ingot wall and thicker sidewall flux layers.

An alternate technique was used when melting larger pieces of scrap, which were difficult to sidefeed with the equipment available. For melting any material which did not sidefeed readily, the sidefeeding tank was equipped with a glove port through which scrap was hand-fed to the vibrating feeder. A container of flux was placed in the sidefeeding tank with the scrap metal, and the flux pool was replenished at intervals whenever the supply of flux in the crucible became depleted. As with turnings, the previously melted scrap required approximately 4 weight-percent of flux.

As soon as the material to be melted had been placed in the sidefeeding tank, the furnace was closed and evacuated. Most melting was conducted at a furnace pressure of $\frac{1}{3}$ atm helium for material which could be sidefed readily and at 1 atm helium when the material was handfed through the glove port.

Melting was initiated by applying power to the work coil until the initial charge of metal and flux melted. Power was limited at the start of melting to insure melting of some flux before melting the metal. In this way, a layer of flux

Table 57.—Weights and dimensions of starting materials for inductoslag melting

Ingot diameter, cm	Starting stub			Initial charge, metal		Initial charge flux kg
	Length, cm	Body diameter, cm	Shoulder diameter, cm	Diameter, cm	Weight, kg	
8.9	11.4–12.7	8.3– 8.6	8.7	5.1– 7.0	0.23	0.34
10.2	12.7–15.2	9.5– 9.8	10.0	6.4– 7.6	0.23– .46	.46
12.7	15.2–20.3	12.1–12.4	12.5	8.9–10.2	.46– .92	.57



Figure 119.—Furnace interior showing crucible, work coil, and side-feeding mechanism.

formed against the wall of the crucible and prevented direct contact between the crucible wall and the ingot. As soon as a portion of the flux had melted, the power was increased until the entire upper surface of the metal became molten. Once a pool of molten metal had been established and all of the initial flux had been melted, sidefeeding of metal and flux was started.

Metal was added to the pool as rapidly as it would melt. If the rate of addition was too great, the pool was flooded with unmelted material, and a bridge, which was often difficult to melt, formed over the pool. These bridges were difficult to remove, particularly when melting sponge or turnings, because they did not heat effectively and were separated from the molten part of the ingot. Raising the ingot carried the bridges farther up in the crucible, while lowering the ingot would sometimes leave the bridged

material behind. Larger pieces of scrap were heated more effectively by the field of the work coil and caused less difficulty. In fact, it was sometimes effective when melting larger pieces to keep unmelted material in the crucible to reduce the problem of splashing when larger pieces were dropped into the crucible.

As metal was added to the crucible and the level of the upper surface of the ingot rose in the crucible, coupling between the work coil and the ingot changed, and the power input decreased. This characteristic of the unit provided a convenient signal for controlling the rate of ingot withdrawal. As metal was added to the crucible, the ingot was lowered at a rate which maintained a constant power input. Changes in ingot level of less than 0.3 cm (0.1 inch) were sufficient to cause a noticeable change in power.

As soon as all the metal had been melted, the

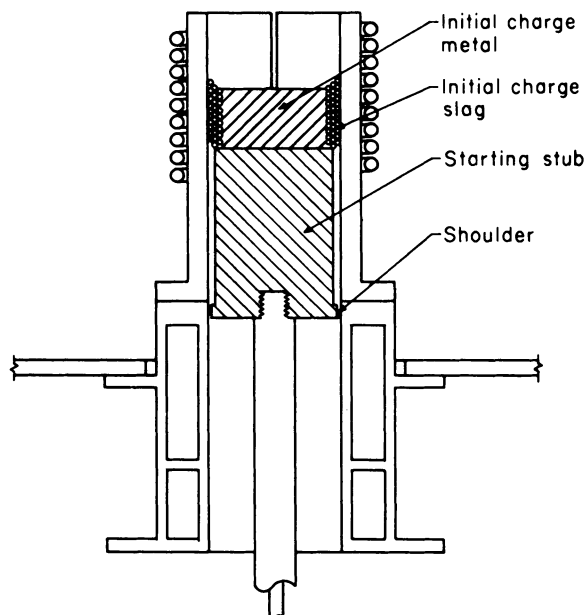


Figure 120.—Initial charge to crucible at start of melting.

power was terminated and the ingot was allowed to cool in the furnace. The flux layer, which formed on the ingot during melting, was easily removed from the ingot. Usually, most of the flux had fallen off the ingot into the bottom of the furnace during melting, and any that remained on the ingot after it was removed from the furnace was easily brushed or chipped off.

Observations During Melting

Strong forces exerted by the field on the molten pool caused the upper surface of the pool to be lifted several inches and to assume the shape shown in figure 117. Molten flux occupied the space between the ingot and the crucible wall at the base of the mound-shaped molten pool. This provided a supply of molten flux at the crucible wall and undoubtedly contributed to the success of the process. Flux which came in contact with the cold wall of the crucible solidified and formed a lining along the wall of the crucible. The ingot was formed within a sleeve of solid flux and did not contact the copper wall. The upper surface of the ingot was raised above the flux layer and was thus exposed to the furnace atmosphere.

Some coupling between the work coil and the metal walls of the crucible was indicated by nonuniform heating of the ingot. More intense

heating of the ingot occurred at the slits, and the pool was distorted by circumferential variations in field strength. Attempts to measure losses to the crucible were unsatisfactory because of the difficulty of differentiating between heat attributed to current flow in the crucible and heat transfer from the ingot. Additional work is needed in this area, particularly as related to elements of crucible design.

When small pieces of metal were sidefed into the crucible, they tended to slide down the surface of the molten pool and collect against the crucible wall. A buildup of this unmelted metal was generally the factor that limited the melting rate. Even though sufficient heat to melt the feed material existed in the pool, these pieces would float on the surface, partially supported by contact with solidified flux or metal at the wall. In time they would be melted, but buildups of this type generally slowed melting.

With larger pieces, the metal added sank into the pool and was more easily melted. The only difficulty with larger pieces was splashing of molten metal when pieces were dropped into the crucible. In some cases, metal would splash against the copper crucible above the flux layer and freeze. When this happened, heat transfer rates to the crucible increased and the efficiency decreased. By adding pieces before the preceding piece had completely melted, this splashing was minimized.

One of the biggest problems encountered has been that of improving the melting rates and decreasing the energy required to melt. Early in this work, it was thought that melting rates would be increased by reducing the height of the coil and thereby reducing the length of the heated ingot from which high rates of heat transfer to the cold crucible would occur. Use of short coils did not result in increased melting rates as expected, and subsequent tests, in which the height of the work coil was increased, have resulted in improved melting rates, particularly when melting turnings and sponge. It is believed that, when melting with short work coils, such a short length of molten metal was obtained that the unmelted portion of the ingot below the pool was exposed at the sidewalls and the metal added stuck to this and did not fall into the pool. With coils which provided good melting conditions, the pool depth was approximately equal to the ingot diameter.

Melting rates are still low compared to those for vacuum-arc melting. Figure 121 shows the

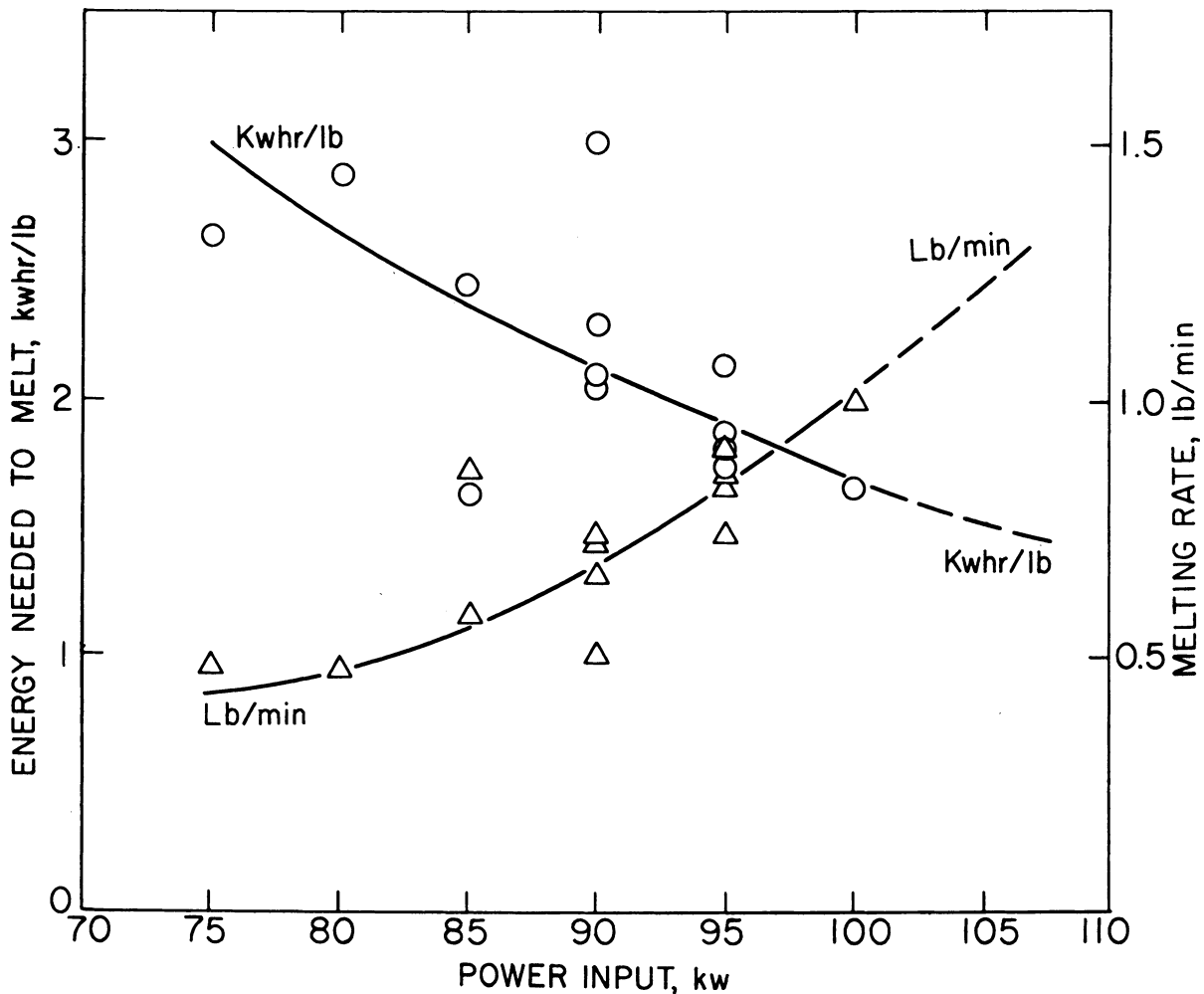


Figure 121.—Relationship between power input, melting rate, and energy needed to melt chopped Ti-16V-2.8Al alloy plate in a 10.2-cm (4-inch) diameter crucible.

relationship between power input and melting rate and between power input and kilowatt-hours per pound of metal melted. These data were obtained by melting 4.5-kg (10-pound) lots of chopped titanium alloy plate in a 10.2-cm (4-inch) diameter crucible. The work coil was nine turns of 1.27-cm ($\frac{1}{2}$ -inch) diameter copper tubing with an overall height of 12.7-cm (5-inches). For these runs a 4.5-kg (10-pound) charge of chopped plate was placed in the sidefeeder along with 0.2-kg (0.4-pound) of calcium fluoride. A molten pool was established in the crucible,

and the time required to completely melt the 4.5-kg (10-pound) charge at a given power level was determined. Power levels were varied from the lowest power that resulted in a reasonable melting rate to the highest power available.

From the trend indicated in figure 121, it is assumed that increased melting rates would be possible at power levels greater than the 100 kw available and that the minimum value for kilowatt-hours per kilogram of metal melted would also occur at some higher power level. These tests were made with the alloy Ti-16V-2.8Al,

which melts more easily than unalloyed titanium. Power requirements for similar tests with unalloyed titanium would be somewhat higher than values given for these tests.

Much has yet to be learned regarding details of crucible design. Two factors believed to influence the melting efficiency of crucibles are wall thickness and number of slits. The thinner the wall, the closer the coil can be to the ingot and the more efficient the crucible will be. Wall thickness must be great enough for water cooling and for adequate strength, however. Also, the more slits in the crucible, the more uniform the heating of the ingot will be. Increasing the number of slits increases the number of water connections and increases the complexity of crucible construction. Slit width and shape may also be factors, but the width must be narrow enough to prevent metal from flowing into the slit. Slits in existing crucibles were approximately 0.25 cm (0.1 inch) wide and would have been more satisfactory at 0.16 cm (0.06 inch) or less. When molten metal ran into the slits, heat transfer to the crucible increased and ingot withdrawal became difficult. At no time were all of the slits electrically shorted, although this possibility exists. If all the slits did short out, heating of the ingot would decrease because of increased attenuation of the field by the crucible.

Under ideal conditions, melting took place within a sleeve of solidified calcium fluoride which formed on the cold wall. This sleeve of flux bridged the slit in the crucible or filled the slit. On occasions, especially when the ingot was raised and lowered repeatedly, this sleeve was broken and molten metal flowed into the slit. Usually only a short tongue of metal ran into the slit before it solidified, but this caused no particular difficulty except to increase heat transfer to the crucible.

Some benefit was also received from thermal insulation of the ingot from the crucible by the solid layer of flux, and best melting conditions occurred when an unbroken sleeve of flux was maintained. While this sleeve of flux was believed to form on the crucible wall, as shown in figure 117, the solidified layer of flux adhered to the ingot and was withdrawn with the ingot.

One problem associated with crucible design was the tendency for the crucibles to become barrel-shaped through prolonged use. The crucible segments were supported at the lower end by the flanged connection to the non-segmented water manifold and at the top with an insulated bolted joint at the slit or an insulat-

ing ring surrounding the segments. After many hours of use, the diameter of the crucible in the melting zone became enlarged, with a resulting increase in the width of the slits. The segments were easily reshaped at intervals by bending, but a better crucible design should be developed to alleviate this problem.

Results

Titanium ingots have been prepared from a variety of starting materials including sponge, machine chips, chopped plate, and large pieces of scrap. All these forms of titanium were melted readily to produce sound ingots.

The ingot shown in figure 122 was prepared from vacuum-distilled titanium sponge by side-feeding. Leached-and-dried titanium sponge was also used to prepare ingots by the same technique. These ingots were melted by first establishing a pool of molten metal and flux in the crucible and then sidefeeding sponge into the pool as rapidly as the sponge was assimilated by the molten pool. Data show that the leached-and-dried sponge, which contains more volatile impurities, had to be melted more slowly, and the ingot prepared from vacuum-distilled sponge had a better sidewall.

Ingot were also prepared from titanium scrap to determine the effectiveness of inductoslag melting for scrap reclamation. The ingot shown in figure 123 was prepared by melting scrap similar to that shown with the ingot. This scrap was reject castings of Ti-6Al-4V alloy. The ingot shown was subsequently used as a consumable electrode in a vacuum-arc melting and casting furnace. Figures 124 and 125 show 10.2- and 12.1-cm (4 and 4¾-inch) diameter ingots also prepared from titanium scrap.

All of the ingots produced by inductoslag melting had relatively good sidewalls and were sound internally except for shrink holes near the upper surface. A longitudinal section of the upper part of a typical ingot prepared from vacuum-distilled titanium sponge is shown in figure 126. The relatively large area of equiaxed grain structure and the shrink hole near the top of the ingot indicate that the molten pool was 7.5 to 9.0 cm (3 to 3½ inches) deep when the run was terminated. No attempt was made to eliminate the shrink hole by hot topping in this run, but hot-topping practices similar to those used for vacuum-arc melting and electroslog melting should reduce the size of these holes or eliminate them entirely. Close examination of figure 126 shows that this ingot was free of the



Figure 122.—Induction-melted 8.9-cm ($3\frac{1}{2}$ -inch) diameter ingot prepared from vacuum-distilled titanium sponge.

subsurface porosity characteristic of first-melt ingots prepared from titanium sponge by consumable-electrode vacuum-arc melting. In this respect, the ingots closely resemble ingots prepared by electroslag melting.

One possible application of inductoslag melting would be as a first-melting step in which loose titanium sponge would be converted into electrode stock for vacuum-arc remelting. Inductoslag melting would eliminate the pressing and welding steps necessary for preparing first-melt electrodes and would also eliminate any machining operations required of first-melt ingots prepared by vacuum-arc melting. To test the possibility of such a melting scheme, ingots were prepared by inductoslag-melting titanium sponge, and these ingots were remelted by conventional vacuum-arc melting. Inductoslag-melted ingots, prepared from either vacuum-distilled or leached-and-dried titanium sponge, were suitable for vacuum-arc remelting without machining of the outer surface.

To further evaluate the potential of this process for melting titanium sponge, ingots were prepared from one lot of magnesium-reduced, vacuum-distilled sponge by both vacuum-arc and inductoslag melting. Conventional double melting was used in preparing the vacuum-arc-melted ingot; single melting was used in preparing the inductoslag-melted ingot. The resulting ingots were evaluated to determine whether single-melting titanium sponge in the inductoslag furnace would produce an ingot comparable to one produced by double-vacuum-arc melting.

The arc-melted ingot was prepared by melting 5.1- by 5.1- by 25.4-cm (2- by 2- by 10-inch) pressed bars of sponge into a 10.2-cm (4-inch) diameter ingot. The first-melt ingot was machined on the outer surface to remove condensed salts and impurities, quartered, and remelted into a 10.2-cm (4-inch) diameter ingot. A forging billet was prepared from this remelt ingot by machining the sidewalls and cropping the upper end to remove the shrink hole.

The inductoslag-melted ingot was prepared from the same sponge lot by single melting, and two forging billets were prepared. One billet was prepared from the upper 20 cm (8 inches) of the ingot. The sidewall was not machined and the shrink hole was not cropped. A second billet was prepared from the lower 25-cm (10-inches) of the same ingot, but the sidewall of this billet was machined to provide a comparison between as-melted and machined sidewalls during forging. Both billets forged equally well.



Figure 123.—Induction-melted 10.2-cm (4-inch) diameter ingot and the type of scrap from which it was melted.



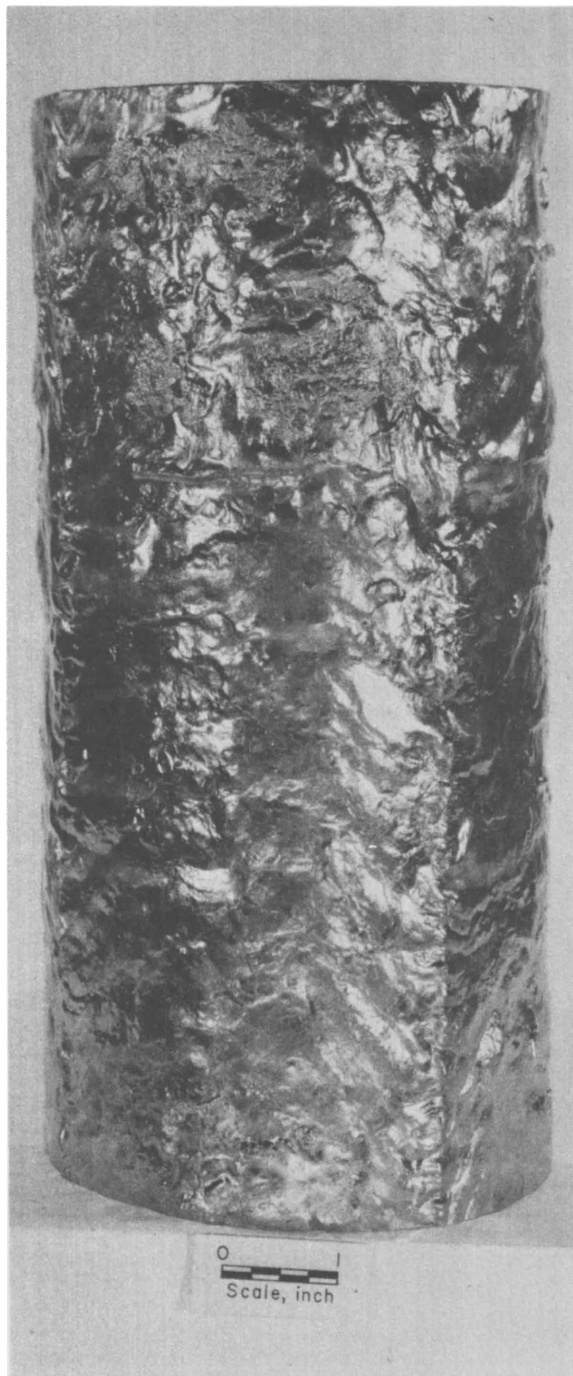


Figure 125.—Section of 12.7-cm (5-inch) diameter ingot prepared from chunks of Ti-6Al-4V alloy scrap.

Hardness values for the three billets are given in table 58. Top and bottom values were from

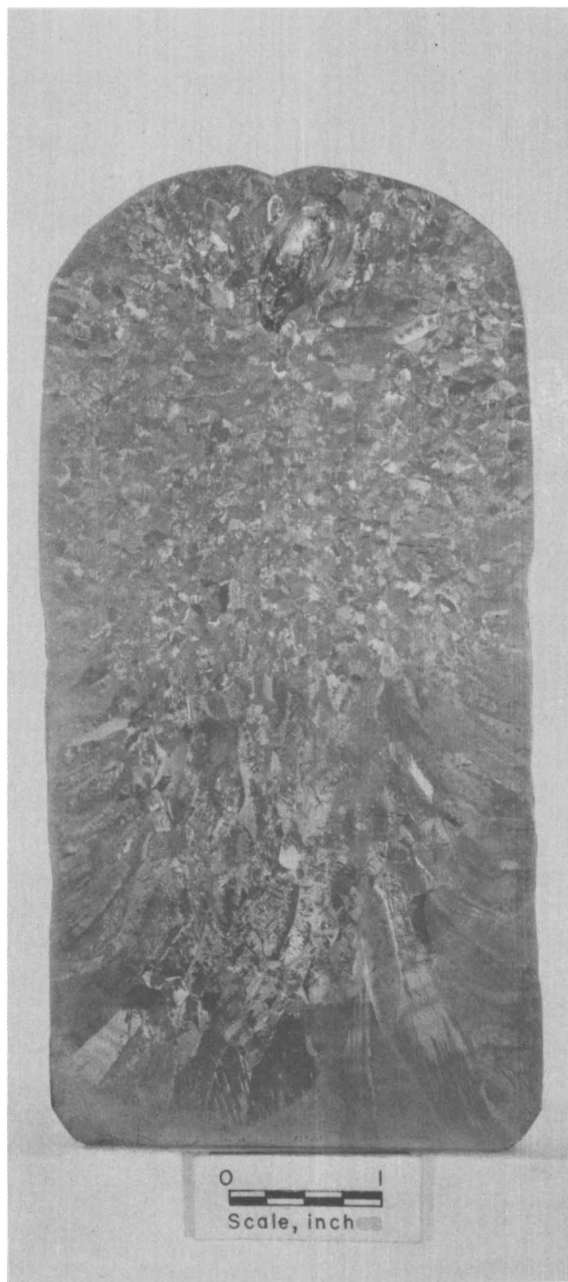


Figure 126.—Macrostructure of 8.9-cm (3½-inch) diameter induction-melted ingot of vacuum-distilled titanium sponge.

the end faces of the billets, and side values were taken at three positions ranging from top to bottom of the billets. Analyses of the ingots from which these billets were prepared and of a sample button of the sponge used are given in table 59. As shown in table 58, the inductoslag-

melted top section was slightly harder than the vacuum-arc-melted ingot, and the bottom end was markedly harder. Similar results have been noted for electroslag-melted ingots. The increased hardness at the bottom was attributed to gettering of impurities from the initial charge of flux by the first metal melted. Unfortunately, samples for oxygen, hydrogen, and nitrogen were not taken from the bottom of the inductoslag-melted ingot, and the analyses obtained do not substantiate the increase in hardness noted. More complete analyses of a larger number of ingots are needed to clarify the effect of inductoslag melting on metal purity; however, several tentative conclusions can be made, based in part on experience gained during electroslag melting.

As discussed in chapters 7 and 8, studies of electroslag melting of titanium demonstrate that, with the exception of reductions in magnesium, chlorine, and sodium, no purification of titanium is achieved by treatment with flux. In fact, any impurities in the flux tend to be getterd by the titanium, and an increase in metallic and interstitial impurities in the titanium can be expected. In addition, titanium melted in fluoride fluxes will invariably contain fluorine. By treat-

ment of the flux as described in chapter 7, impurities in the flux-melted titanium can be held to a minimum.

Little difference was noted in the hydrogen content for ingots prepared by vacuum-arc melting and inductoslag melting because of the relatively low level of hydrogen in the sponge. Inductoslag melting was not effective in removing hydrogen from sponge with a high hydrogen content, however.

Since the values listed in table 59 represent analyses of a single ingot prepared by each melting technique and some scatter of analytical data is normal, we do not consider any individual analysis significant beyond that already discussed.

All three billets were hot forged at 900° C (1,650° F) to 5.1- by 10.2-cm (2- by 4-inch) bar, hot rolled at 900° C (1,650° F) to 1.27-cm (1/2-inch) thick plate, and annealed at 704° C (1,300° F) for 25 minutes. Tensile specimens and V-notch Charpy impact specimens were machined from the upper portion of the plate produced from each of three billets. Results of tests are given in table 60. Tensile properties of plate produced from inductoslag-melted sponge reflect

Table 58.—Brinell hardness of forging billets prepared from vacuum-distilled titanium sponge by vacuum-arc melting and by inductoslag melting

Billet	Brinell hardness number, standard ball, 3,000 kg load					
	Top	Side	Side	Side	Bottom	Average
Vacuum-arc melt SA 27588	174	134	131	137	146	144
Inductoslag melt 192:						
Top section	146	146	152	149	140	147
Bottom section	140	156	156	179	179	162

Table 59.—Analyses ¹ of ingots prepared from vacuum-distilled titanium sponge

Sample	C	H	N	O	F	Al	Ca	Cr	Cu	Fe	Mg	Mo	Si	Sn
Sponge sample	194	17	48	764	(²)	<10	<10	<10	10	30	<5	<15	<30	100
Vacuum-arc-melted ingot ³														
Top	98	23	72	858	(²)	<10	<10	<10	50	50	<5	<15	100	200
Bottom	164	ND	ND	ND	(²)	10	<10	<10	50	300	<5	<15	20	200
Inductoslag-melted ingot ³														
Top	122	25	44	865	20	10	30	10	100	500	10	30	500	500
Bottom	139	ND	ND	ND	25	20	<10	10	50	500	5	50	500	200

ND Not detected.

¹ O by inert gas fusion, H by hot extraction, N by Kjeldahl, F by sensitive electrode method, C by combustion, all others by optical emission spectroscopy.

² Fluorine analyses not obtained. In previous fluorine analyses of vacuum-arc-melted ingots prepared from this sponge lot, fluorine was not detected.

³ Turnings samples for C, F, and metallic impurities are taken from top and bottom of ingots; samples for H, N, and O were taken from top of each ingot only.

the slightly higher impurity levels. Lower impact strength of material prepared by inductoslag melting was also noted. Similar results were noted for electros slag-melted titanium as described in chapter 9.

As Schipperit's work (16) indicated that 6.4-cm (2½-inch) diameter ingots could be melted in crucibles of the type used in this work but without flux, one run was attempted in this equipment without flux. This run differed from other runs made with loose sponge only in the absence of flux. As soon as a pool of molten metal formed and molten metal ran against the sides of the crucible, heating of the metal decreased, and it was impossible to maintain a full pool of molten metal. Sponge added to the crucible by side-feeding did not melt completely.

When the metal was removed from the crucible, evidence of arcing between adjacent segments of the crucible was noted. The slits in the crucible were pitted at the level of most intense heating, and metal which had melted had run into the slits in the crucible. No further attempts were made to operate without flux because of the negative results obtained during this run.

Additional work is needed to improve crucible design, melting rates, and energy required for melting. Tests with large-scale equipment of this type, particularly melting large-diameter ingots with low-frequency power supplies, are needed but are considered beyond the scope of Bureau of Mines research. Current efforts by the Bureau of Mines are directed toward the application of

this melting technique to the production of shaped castings.

PLASMA ELECTROSLAG MELTING

An alternate method for eliminating the consumable electrode in the electros lag process involves an ionized gas column or plasma to transfer high-powered ac current from a relatively low-power torch to the flux bath. This scheme was developed by Electros lag Refining Technology (ESRT), a development unit of BISRA in Great Britain. (See chapter 1.)

The plasma torch is composed of a water-cooled copper electrode with a tungsten tip (dc negative), which is surrounded by a water-cooled copper shell (dc positive) with a constricted orifice. An inert gas, which is usually argon or an argon-nitrogen mixture, is ionized by an arc discharge and produces the plasma. An ac voltage is applied between a water-cooled insulated base plate and the shell so that the plasma can support a large current which, in turn, melts the flux. Powders, scrap, or liquid droplets can then be introduced into the flux bath and arc melted to form an ingot. Small-scale ingots (~10-cm or 4-inch diameter) of a wide variety of metals have been prepared by this technique (7).

CONTINUOUS ELECTROSLAG MELTING

During research on electros lag welding thick plate, a technique utilizing a continuous fixed electrode and powder was evolved at the Arcos Corp. in Belgium and the United States. In this

Table 60.—Average ¹ tensile properties and impact strength of annealed plate prepared from vacuum-distilled titanium sponge

Billet	Orientation	Tensile strength, psi ²	Yield strength, 0.2-pct offset, psi ²	Elongation, pct	Reduction in area, pct	Impact strength, ft lb ³
Vacuum-arc melt SA 27588	Longitudinal	57,300	41,500	33	73	170
	Transverse	57,600	48,400	32	70	175
Inductoslag melt 192: Top section	Longitudinal	61,100	48,400	31	65	92
	Transverse	59,900	52,700	30	63	130
Bottom section	Longitudinal	65,400	49,200	29	62	91
	Transverse	60,500	52,300	30	61	131

¹ Average of 3 test specimens.

² To convert to approximate kg cm⁻², multiply by 0.07.

³ To convert to Joules, multiply by 1.3558.

process, a continuous wire or killed mild steel strip electrode (3.8- by 0.09-cm to 76.2- by 0.20-cm) or 1.5- by 0.04 to 30- by 0.08-inch, which is surrounded by metal alloying powder (similar to the original Hopkins process; see chapter 1), is fed into the molten flux bath. Controlled amounts of powders (from 2.3 to 4 times the amount of the wire or strip and with a grain size from 0.05 to 0.3 cm or 0.02 to 0.1 inch) are introduced onto the current-carrying portion of the electrode above the molten fluorite-lime-alumina flux. The powders can also be premixed. Such powder adheres to the strip due to the surrounding magnetic field produced by a high-density current flowing through the electrode. This causes intense heat, small molten droplet size, and an electromagnetic stirring action. During melting, the electrode oscillates across the entire flux pool, exposing uncontaminated flux to the melting metal. This oscillation also encourages uniform heat distribution and deposits the alloying powder uniformly across the flux bath, thus improving solidification by producing a flat molten metal pool. The flux is automatically replenished and tapped for constant purification potential.

The ingot (ranging from 10.2 cm or 4 inches square to 100 cm or 39 inches in diameter by 45 cm or 17 inches long) forms in a water-cooled copper crucible with an open bottom and descends at a rate of 1.27 to 4.81 cm min⁻¹ (0.5 to 1.9 inches min⁻¹). It can be cut off by a torch at desired locations. A high degree of chemical homogeneity is claimed (8, 11, 13) with a 98-percent yield for stainless steels. In addition, maraging steels and a copper alloy have been successfully melted by this process. Microstructures typically show a fine, uniform grain size with nearly complete absence of nonmetallic inclusions.

Advantages claimed for the process over the conventional electroslag process include (1) continuous operation, (2) lower power consumption (approximately half), (3) 20 times greater flux-metal contact surface, and (4) flux stirring (19).

At present, Belgian workers are concentrating on scaling up to produce 20- to 50-ton ingots; the eventual goal is 120- to 132-ton ingots (5, 11). Annular molds have also been developed (5).

MODIFICATIONS TO THE ELECTROSLAG PROCESS

Electrode

Two variations in electrode design for electroslag melting have been described in the litera-

ture. The first is the use of multiple electrodes to produce slabs or tubular ingots. Usually, three electrodes connected to a three-phase ac power supply are used. Successful operation requires adequate crucible-electrode clearance, correct electrical conditions, and equal melting rates for each electrode. However, these requirements are difficult to achieve. Ingot shapes with the electrodes in a row or in a triangular configuration are produced only with low power efficiency. High furnace reactance is also a problem. To alleviate these problems, Soviet metallurgists have developed a bifilar system for single-phase ac-powered furnaces. Two consumable electrodes connected in series are fed into the flux bath at an identical rate by a single electrode holder. The two current leads are electrically insulated from one another. This scheme is said to significantly reduce the inductance and the power consumption, and is suitable for producing large slab-shaped ingots. Electrode complexity and furnace dimensions, however, are substantially increased. Further details and favorable melting experiences have been described in the literature (10, pp. 189-235).

The second electrode modification was also developed in the Soviet Union and involves the use of a fixed electrode. In this scheme, the height of the ingot increases during melting while the length of the electrode decreases as it is consumed. As the melt progresses, the flux depth increases to compensate for the variation in changes in the lengths of the electrode and ingot. Thus, electrode drive mechanisms are eliminated (10, pp. 239-250).

Some comments with regard to current paths as a function of furnace and/or electrode design are also relevant. In the case of a live mold, the full working current enters the electrode, travels through the slag and metal, and is then carried through the mold wall. In this case the ingot-mold electrical resistance is near zero. In the case of an insulated mold, the ingot-mold electrical resistance is usually greater than 10 k Ω , although a small portion of the working current leaks through. In the live mold configuration, the risk of wall puncture is greater, large stirring effects are present, and the potential gradient in the slag is less uniform than in the case of an insulated mold.

In three-phase ac electroslag operation, the current path travels from three legs of a transformer secondary to three electrodes, through the flux and metal, and back. However, this limits the versatility in producing square and

rectangular ingots because of temperature gradients in the molten flux. The necessity for low fill ratios and high electrode lengths increases the reactance. If the three electrodes are alined in a row, misalignment of phase voltages and non-uniform electrode melting may result. To alleviate these problems, the development of bifilar electroslag melting was undertaken in the Soviet Union as mentioned previously. In the bifilar configuration, current can flow between the electrodes along several paths (between the electrodes entering the slag, from one electrode to the metal pool to the other electrode, and from one electrode to the mold wall and to the other electrode). Pocklington (15) has determined the current paths in such a mode in a small electroslag unit with separate drive controls for each electrode to minimize the effect of uneven consumption rates. When the electrodes were deeply immersed in the flux, the effect of the electrode separation on overall electrical resistance was most pronounced. When the electrodes were barely immersed in the flux and were spread ~ 10 cm apart, 55 percent of the current flowed from the bottom electrode face, whereas when the electrode separation was 2.5 cm, 50 percent of the current flowed directly through the flux to the other electrode. With deeper immersion, over half of the current flows through the flux from one electrode to the other, regardless of electrode separation. Generally, the effective current path is governed by electrode separation and penetration, the fill ratio, and the resistivity and quantity of flux.

Molds

Multiple electrodes connected to a common single-phase ac electrical supply and feeder holder can also operate in separate crucibles. ESRT in Great Britain and Consarc in the United States have successfully melted ingots with this technique. This modification is especially useful in producing small ingots since it fully utilizes available power (3, pp. 127-128).

Another ESRT development involves the use of a reciprocating baseplate. A movable plate is operated by a pneumatic or hydraulic drive in two directions at right angles. The speed and stroke length are widely variable. With such a motion of the baseplate, metal can be deposited over a wide area of the bath using a lower than normal current without degrading the ingot surface. The resulting shallow molten pool promotes axial grain growth in the ingot. The

stirring effect may also enhance refining and ingot homogeneity.

To avoid excessively long crucibles in the production of long ingots and/or if a semicontinuous electroslag operation is desired, two variations in mold design may be used. These include (1) a mold which is driven upward at a rate compatible with the rate of ingot formation, and (2) a mold with a retractable baseplate which can be driven downward to maintain a constant flux level as the ingot is formed. Ingots produced by these methods are comparable in quality and cleanliness to those prepared by the conventional electroslag process (22).

There remains much to learn about the comparison between conventional or static-versus movable molds in the electroslag process. When a movable crucible is used, the ingots characteristically possess rippled and folded surfaces which are not suitable for direct working. This can be alleviated by maintaining a high flux temperature using additional power input since the rough ingot surfaces usually result from uneven heating. Alternatively, electrode fill ratios can be lowered, which increases power consumption and pool depth. These disadvantages can be at least partially offset by the use of high-resistivity fluxes. Another problem when using movable crucibles is control of runouts, which can also be minimized by a low fill ratio. The greatest advantage in using movable molds is that it permits continuous ingot production, where an ingot must be melted from two or more electrodes, and where the ingot must possess a high length-to-diameter ratio.

During an electrode change operation, a power interruption is inevitable. The resulting unsteady state heat balance and lack of feed metal may be characterized by the volume fraction of liquid solidified during the interruption (9). Either changes in ingot structure or the presence of surface defects have been reported as a result of electrode change operations which provide local temperature gradients and changes in rates of solidification. For each furnace installation and ingot composition, there is a maximum tolerable period for electrode changing. These disadvantages must be weighed against certain advantages; for example, it is convenient to electroslag-melt short electrode lengths and to produce very long ingots where furnace head room is minimal. Jackson, Mitchell, and Luchok (9) have concluded that the applicability of electrode change operations is limited over a great range of sizes and compositions.

Alternative mold cooling techniques to reduce the hazards of explosions have also been developed. These usually consist of a refrigeration system encircling a copper mold which has been machined from a solid copper block.

In recent years, electroslag technology has advanced to the point where numerous ingot shapes are possible. For example, rolling mill rollers can be prepared in a crucible with a hole cut in the bottom to accept molten metal which forms the roller neck. Hollow ingots have been produced by the electroslag process using a truncated conical moving mandrel with two electrodes (wire or rod), a movable or stationary metallic mandrel with one large solid electrode (2; 10, pp. 250-255), or a hollow electrode with stationary or movable mandrels (2). All of these techniques possess inherent disadvantages, such as flux and metal contamination by nonmetallic mandrels, sticking mandrels, and the high cost of complex electrode fabrication. Large rectangular steel plate ingots with dimensions up to 148 by 64 by 1900 cm (58 by 25 by 748 inches), which possess good surfaces and a minimum of inclusions, have been successfully electroslag-melted

by the bifilar technique in the Soviet Union (4, 14).

Flux

To produce electroslag-melted ingots with sound bottoms to minimize cropping losses, a molten flux start is preferred for most high-melting steels and superalloys. This also eliminates the time required to melt a solid flux before the metal can be melted. Flux hydrolysis and contamination are also avoided. The flux can either be melted by a separate nonconsumable electrode or poured into the furnace from an auxiliary arc or induction furnace. Unfortunately, these schemes do not prevent some flux solidification prior to initiation of melting. Accordingly, both ESRT in Great Britain and the Paton Electric Welding Institute in the U.S.S.R. have developed a technique whereby the molten flux is poured into the bottom of the mold through a sidearm. Enough molten flux is siphoned into the crucible to attain the desired level prior to initiation of melting. Increased productivity, the lack of a required baseplate, rapid start, and elimination of arcing are cited advantages (7; 10, pp. 181-188).

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CHAPTER 17.—FUTURE PROSPECTS FOR THE ELECTROSLAG PROCESS

By R. H. Nafziger

Initial acceptance of the electroslag process has been slow, as is often the case when innovative techniques are introduced. Although most of those involved with basic developments of the process believe that acceptance of electroslag melting will increase in the years ahead, actual producers are somewhat more skeptical (6). Future acceptability of the electroslag process will depend largely on comparative costs of comparable techniques, proven advantages and capabilities of the process, improvements in equipment, melting techniques, and fluxes, and practical modifications.

COSTS

Comparative cost estimates between vacuum-arc and electroslag melting processes are difficult to define because of the wide variation in labor costs, overhead, capital costs, and depreciation throughout the world. This is evident from an inspection of table 61 which shows published estimated costs of vacuum-arc and electroslag melting. Perhaps the greatest single cost item in both processes is electrode material and fabrication. It has been estimated (3) that forged electrodes cost approximately 1.3 as much as conventionally cast electrodes. Latash and Medovar (10) claim that rolled electrodes cost less than either forged or cast electrodes, based on Soviet technology.

The figures given in table 61 are considered only rough approximations since plants are reluctant to divulge costs. In addition, the electroslag process is considered still in its infancy, since production experience is relatively limited. However, it appears that costs of electroslag-melted ingots are comparable to those of ingots melted by the vacuum-arc process. It is reasonable to expect that electroslag process costs should be reduced as inevitable technological improvements are introduced.

PARAMETER VARIATIONS

The major parameter which sets the electroslag

melting process apart from more conventional secondary melting techniques is the presence of the flux. In large part this is responsible for the great flexibility of the process, which in turn is attractive to various producers and will probably be responsible for the anticipated growth of electroslag melting in the future. Duckworth and Wooding (5) emphasized the wider variety of adjustable parameters offered by the electroslag process, in contrast to the vacuum-arc process. These include the use of single- and three-phase ac power as well as dc, multiple electrodes which may be variable in shape, nonconsumable electrodes, continuous ingot withdrawal capability, special molds to produce ingots of unusual shapes and/or sizes, and tailored flux composition.

INGOT SIZE

Considerable emphasis has been placed in the past few years on increasing the size of electroslag-melted ingots. With present technology and sophistication, it has been stated that the vacuum-arc process has reached its maximum size capabilities, from an economic standpoint (2). It is anticipated by many people that extremely large ingots will be electroslag melted at costs approaching \$50 per ton.

Flux-metal reactions in melting ingots up to 300 cm (118 inches) in diameter are not expected to change appreciably from those observed in melting ingots up to 100 cm (39 inches) in diameter (7). Wooding and Mowat (14) have recently outlined a number of questions which must be answered with respect to large ingots before significant acceptance of the electroslag process can be envisioned for the future. These involve (1) the nature of the ingot solidification pattern, (2) melt rates, (3) hydrogen control, (4) prevention of thermal cracking, (5) electrode manufacture, (6) design and operation of the furnace, and (7) cost. Their answer is a completely enclosed furnace utilizing a desiccated

Table 61.—*Estimated costs per metric ton of ingot*¹

Ingot size, diam	Vacuum arc	Electroslag	Remarks	Year and reference
NA	NAp	~\$86.24	1 furnace manufacturer.	1967 (11)
NA	NAp	~128.13	Wiggin-Ni alloys	Do.
NA	NAp	98.00	Soviet	Do.
61 cm	\$74.80	72.60	(² ³)	1968 (5)
~20 cm	NAp	83.60	6 furnace—high-speed steel. ...	Do.
~20 cm	NAp	55.00	Multiple ingots—high-speed steel.	Do.
63.5 cm	90.20	77.00	(⁴)	1968 (8)
NA	NAp	79.20	(²)	
NA	NAp	36.52	Optimum objective	1969 (9)
63.5 cm	NAp	59.40	None	1969 (13)
NA	78.93	61.61	Steel EI 961 (12Cr, 2Ni, 0.1C).	1970 (10)
30 cm	NAp	~180.00	Actual total costs	1973 (4)
60 cm	NAp	~ 90.00	Bofors' plant (see chapter 1) ...	Do.
80 cm	NAp	~ 84.00	 do.	Do.
100 cm	NAp	~103.00	 do.	Do.

NA Not available. NAp Not applicable.

¹U.S. dollar costs have been converted from foreign currencies at rates of exchange in effect at the time the figures were originally published.

² Molten flux start.

³ Excluding electrode costs.

⁴ Dry flux start.

atmosphere to minimize hydrogen pickup, and a molten flux start. Uninterrupted melting and maximum ingot yield are achieved by horizontal casting of full-length electrode segments which are melted into uniquely designed crucibles. These authors state that this scheme might be applied to the manufacture of 300-ton forging ingots at an all-inclusive estimated cost of \$71.50 per ton. Other electroslag melting schemes for large ingots use multiple electrodes which require changing during the melt. These techniques are used in open-air melting. Soviet investigators have developed a multiple-electrode melting technique in which six or seven electrodes are arranged in a cluster. No electrode changes are required, and the crucible of special configuration moves upward as the ingot grows so that neither the electrode nor the ingot moves. If these unique schemes can successfully resolve the aforementioned problems, acceptance of the electroslag process for producing large ingots may become a reality, accompanied by a very large growth for the process.

ELECTROSLAG CASTING

One of the unique features of the electroslag melting process is the ability to melt or cast ingots in a variety of shapes. Soviet investigators (1) have devised a method wherein the flux is melted in a crucible, molten metal is poured through the flux, and the ingot is heated by

either a consumable or nonconsumable electrode. This process is said to eliminate shrinkage and has been applied to carbon, tool, ballbearing, heat-resisting, stainless, and low-carbon steels. The most satisfactory flux used was $\text{CaF}_2\text{-Al}_2\text{O}_3$ in the weight ratio of 70:30, with the addition of up to 8 to 10 weight-percent CaO . This process can employ a movable or a stationary mandrel for the production of hollow castings (12). Parts of high-pressure vessels and valves have been successfully cast. The method can also be used to cast crankshafts, cold-rolling rollers, and propeller shafts. If new techniques such as this can be applied to commercial production with costs comparable to those of conventional melting methods, the growth of the electroslag process appears assured.

CONCLUSIONS

Although it is unlikely that the electroslag process will replace vacuum-arc melting, especially in the United States, there is no reason to doubt that the two processes will effectively complement each other in the future. On the basis of cost alone, there is no reasonable justification for replacing existing vacuum-arc facilities with electroslag furnaces. However, the advantages of the electroslag process enumerated throughout this Bulletin should guarantee continued acceptance and growth for the process as new secondary-melting facilities are built and

producers become more acquainted with the unique capabilities of the process. Electroslag process growth will also depend on how well the products conform to increasingly severe specifications for secondary-melted material. In the 10

years from 1960 to 1970, the annual worldwide production of electroslag ingots increased from 100,000 tons to 500,000 tons (4). This represents a steady, linear growth rate which should continue in the future.

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¹ Titles enclosed in parentheses are translations from the language in which the item was published.

